NASA CONTRACTOR REPORT

NASA CR-274

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ULTRA THIN GAUGE POLYMERIC FILMS FOR SPACE APPLICATIONS

by Dale W. Cox, Jr.

Prepared under Contract No. NAS 7-274 *by*
SEA-SPACE SYSTEMS, INC.
Torrance, Calif.
for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • AUGUST 1965

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Contract No. NAS 7-274

SUMMARY

Producing polymeric films almost an order of magnitude thinner in gauge than available heretofore was a prime result of this program. These ultra thin gauge (UTG) films have important space age applications, from improving passive communications satellites to demonstrating great potential as flexible materials in cryogenic applications.

Decreasing the weight and increasing the strength of any engineering material are desirable, but generally, mutually exclusive goals. The UTG films extruded under this contract displayed this anomaly. Layflat tubular polyethylene film in gauges down to 1/16.3 mil (1.55μ; 15,500 Å; or 6.1×10^{-5} in.) was extruded using experimental resins and special equipment for this program. The ultimate tensile strength of the UTG film was 7,550 psi, an increase of almost 300% over conventional gauge film from this same resin. A theory to explain the anomaly has been developed.

The extrusion techniques developed and the equipment modifications required were extensions of previous Sea-Space Systems technology in this area. Detailed discussions of both theoretical limitations, practical problems involved and equipment requirements are discussed. Film test results are presented.

INTRODUCTION

Extruding extremely thin polymeric films is a time-consuming, laborious art. Frequent die blowouts, many times for which no reasonable explanation can be derived, are the general rule using existing commercial equipment. This, of course, is simply because commercial equipment has not been designed for this application. The thinnest gauge films produced by industry are generally .38 mil to .40 mil. Seldom is film produced less than 1/3 mil, particularly in polyethylene. The cost of any polymeric film rises rapidly with a decrease in gauge, sometimes by a factor of 3 or 4. Also, since the polymeric film business is highly competitive, the overriding criteria for most installations is producing "pounds per hour" of film, or "dollars per hour", with little interest in optimizing the equipment for any other objective.

Sea-Space Systems had extruded 0.1 mil polyethylene (PE) film prior to this program, and had outlined the problem areas with sufficient detail to be reasonably confident that much thinner gauge films could be extruded.

Achieving very thin gauge film would be of definite benefit to several programs and missions of NASA. For example, a passive communications satellite appears feasible using UTG composite films in which the diameter can be increased from 135 feet to 425 feet, providing improved electronic response at very little increase in weight.

The specific process involved in this project for extruding ultra thin films was a vertical, blown film process, including a conventional long barrel extruder, variable orifice die, and high tower takeup. In this blown-film extrusion process, molecular orientation is achieved in both the machine and transverse directions, the relative degree depending primarily on the draw ratio (die opening to film gauge) and the blow-up ratio. The results, in general, are films with approximately balanced strengths in both directions, with good physical properties and sealability.

In studying the theoretical aspects of ultra thin gauge films, and the extrusion processes themselves, references (a) through (g) were used. However, apparently no one in the literature has addressed themselves to very thin polymeric films or any aspect of their production, properties, uses or advantages.

In consideration of the foregoing, a NASA study control was originated to determine the feasibility of producing ultra thin gage films in practical quantities.

TECHNICAL DISCUSSION

Study Phase

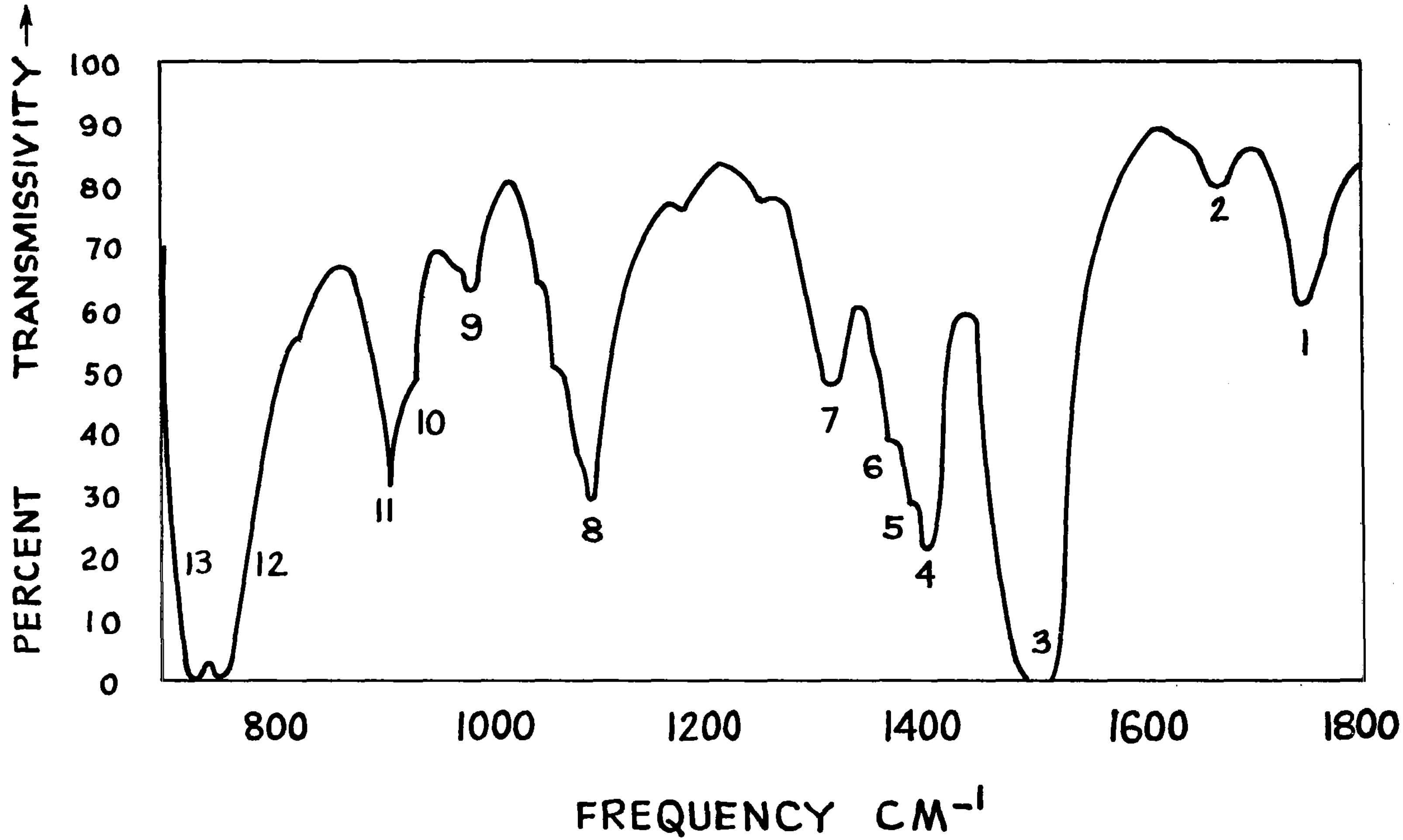
The theoretical limitations of extruding UTG films, exclusive of any mechanical equipment requirements, are associated with the molecular weight distribution, chain length and structure of the molecules. If the extrudate could be homogenously extruded with no mechanical problems, the limitation in gauge is simply a function of the complex relation between the average molecular weight, the molecular length and the chain branching.

From the various methods of film preparation it can be expected that any specimen of polyethylene will contain molecules of a wide range of sizes. It is evident, therefore, that for an adequate description of the molecular structure, it is necessary to know not only the proportions of the various chemical groups but also the average molecular weight and the distribution of molecular weights. Moreover, it would be convenient to know not only the frequency of the branch points but also the distribution of branch lengths. Data of this nature is extremely difficult to obtain. Since this cannot be determined precisely for the film extruded in this program, a general approach will be used.

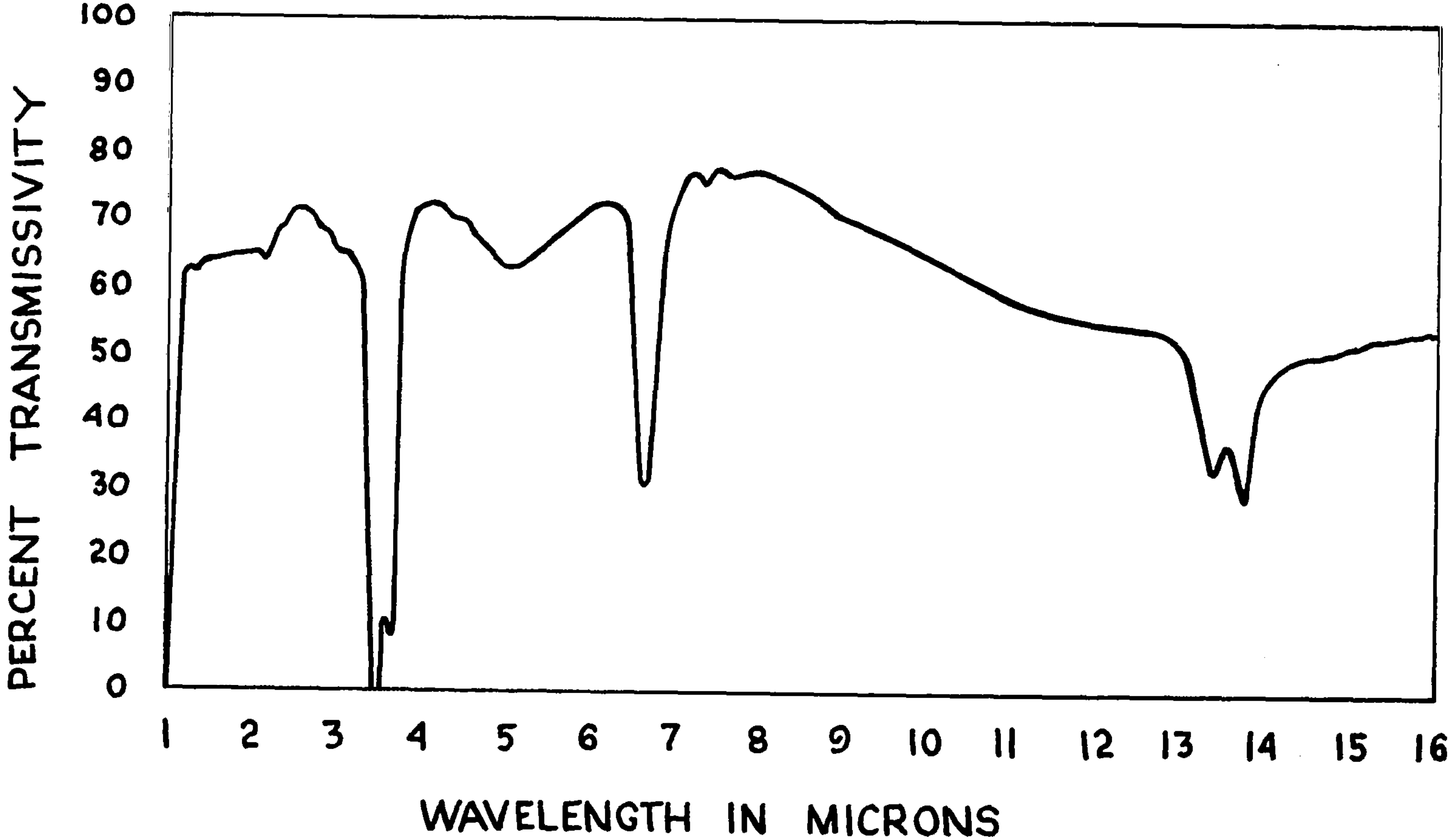
Knowledge of the molecular structure of polyethylene rests almost entirely on evidence derived from physical, as opposed to chemical methods. Chemical analysis tells us little more than that the empirical formula of polyethylene is substantially $(CH_2)_n$. The only other element present in detectable proportion in polyethylene is oxygen in minute amount, derived from the catalyst. With some difficulty, elements present can be estimated by chemical methods but infrared absorption spectrometry is required to establish the manner in which it is linked chemically. Polyethylenes made by low pressure processes may give very small amounts of ash, in which certain metallic elements (derived from the catalysts) can be detected. The amounts of elements other than carbon and hydrogen are so small that they can have little influence on most properties of the polymer.

Infrared absorption spectra (see attached figure) show very strong bands which leave no doubt that the molecules consist for the most part of CH_2 chains: there are the C-H stretching bands of the CH_2 group at 2, 850 cm^{-1} (symmetric stretching) and 2, 926 cm^{-1} (asymmetric stretching), a doublet at 1, 464 and 1, 473 cm^{-1} due to symmetric deformation, and a doublet at 720 and 730 cm^{-1} due to asymmetric deformation.

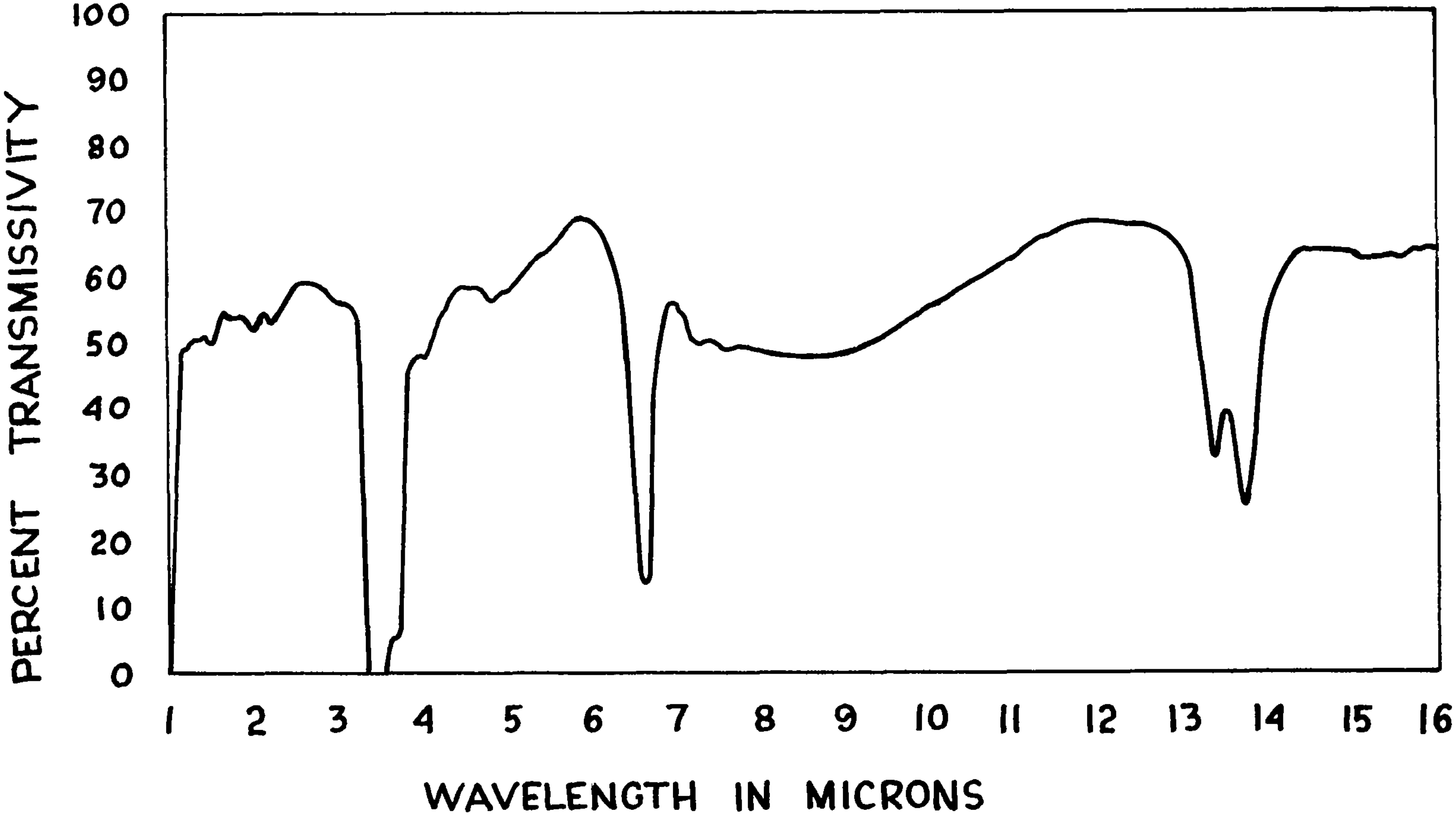
Infrared scans, using a Beckman IR-4 Spectrophotometer, were made of the four principal films produced in this project. (See attached figures).



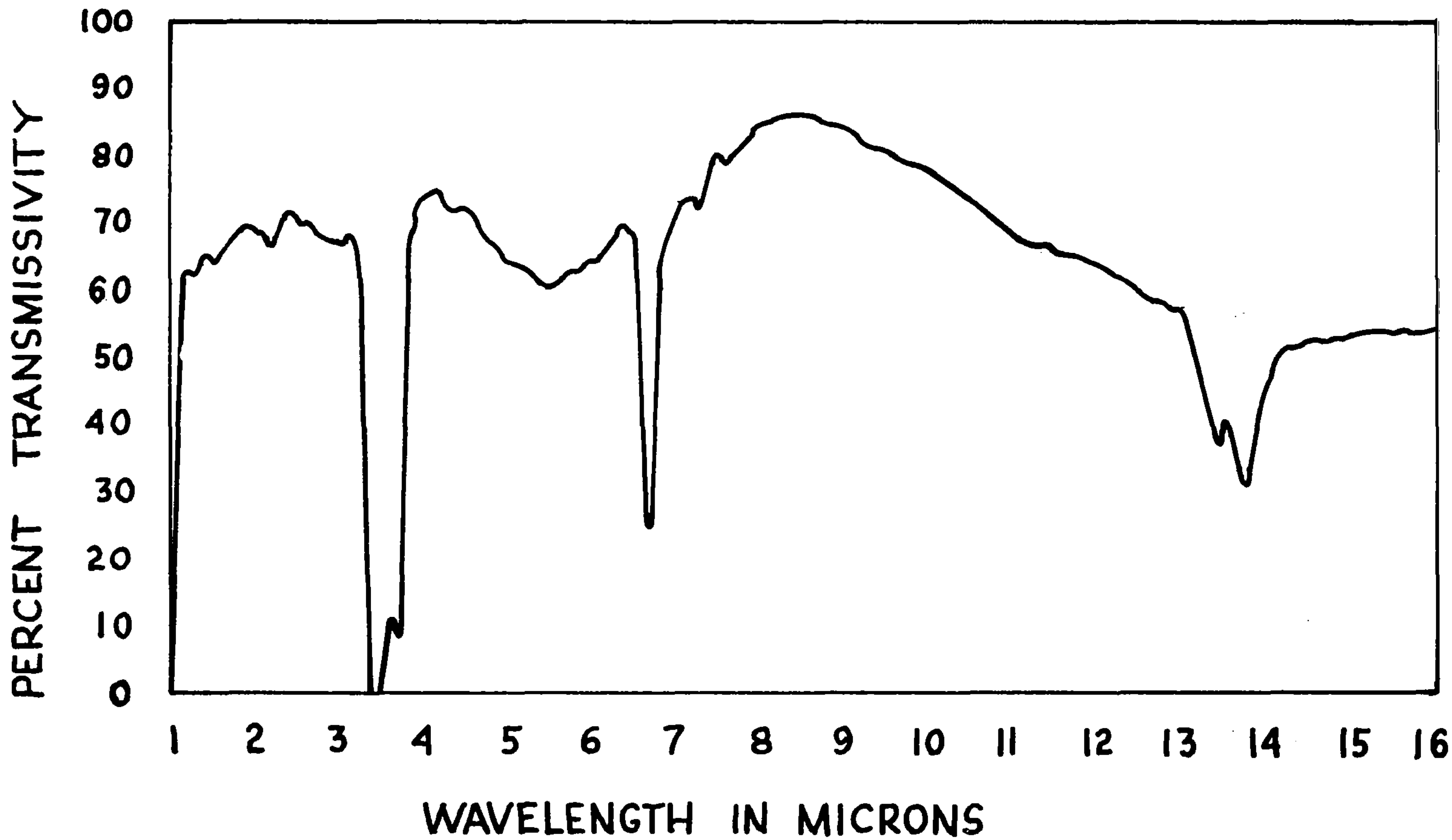
Infrared transmissivity spectrum for polyethylene. Peaks: (1) C=O stretching; (2) C=C stretching; (3) CH_2 symmetric deformation; (4) CH_3 symmetric deformation; (5)-(6) CH_2 wagging (amorphous); (8) C-C stretching; (9)-(11) CH out-of-plane deformation; (12) CH_2 rocking in crystal, polarized along "a" axis, (13) CH_2 rocking in crystal, polarized along "b" axis.



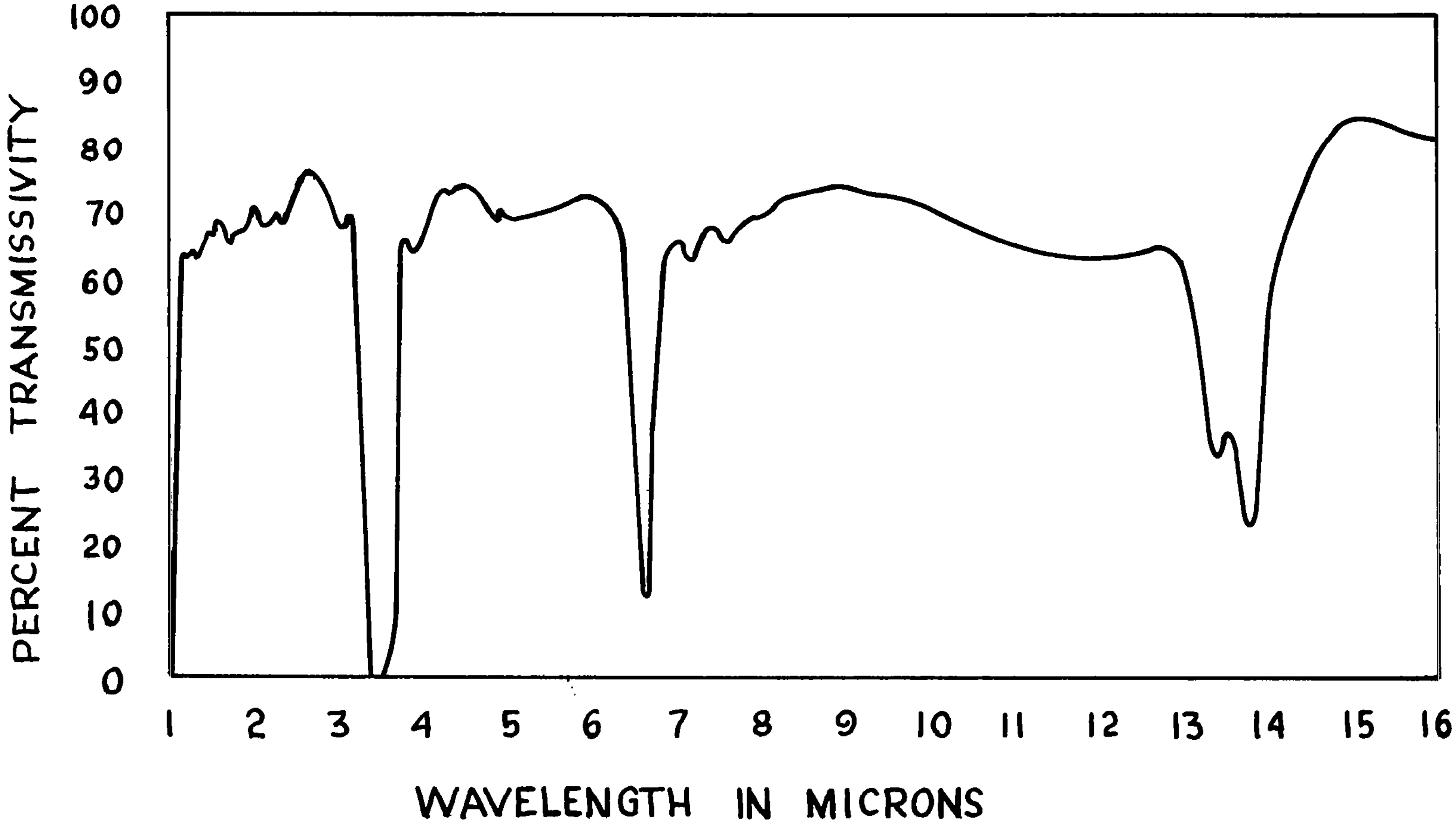
IR SPECTROPHOTOMETER SCAN OF
FILM EXTRUDED FROM DEX 8025



IR SPECTROPHOTOMETER SCAN OF
FILM EXTRUDED FROM DEX 8026



IR SPECTROPHOTOMETER SCAN OF FILM EXTRUDED FROM DEX 8028



IR SPECTROPHOTOMETER SCAN-FILM
EXTRUDED FROM SSS STANDARD

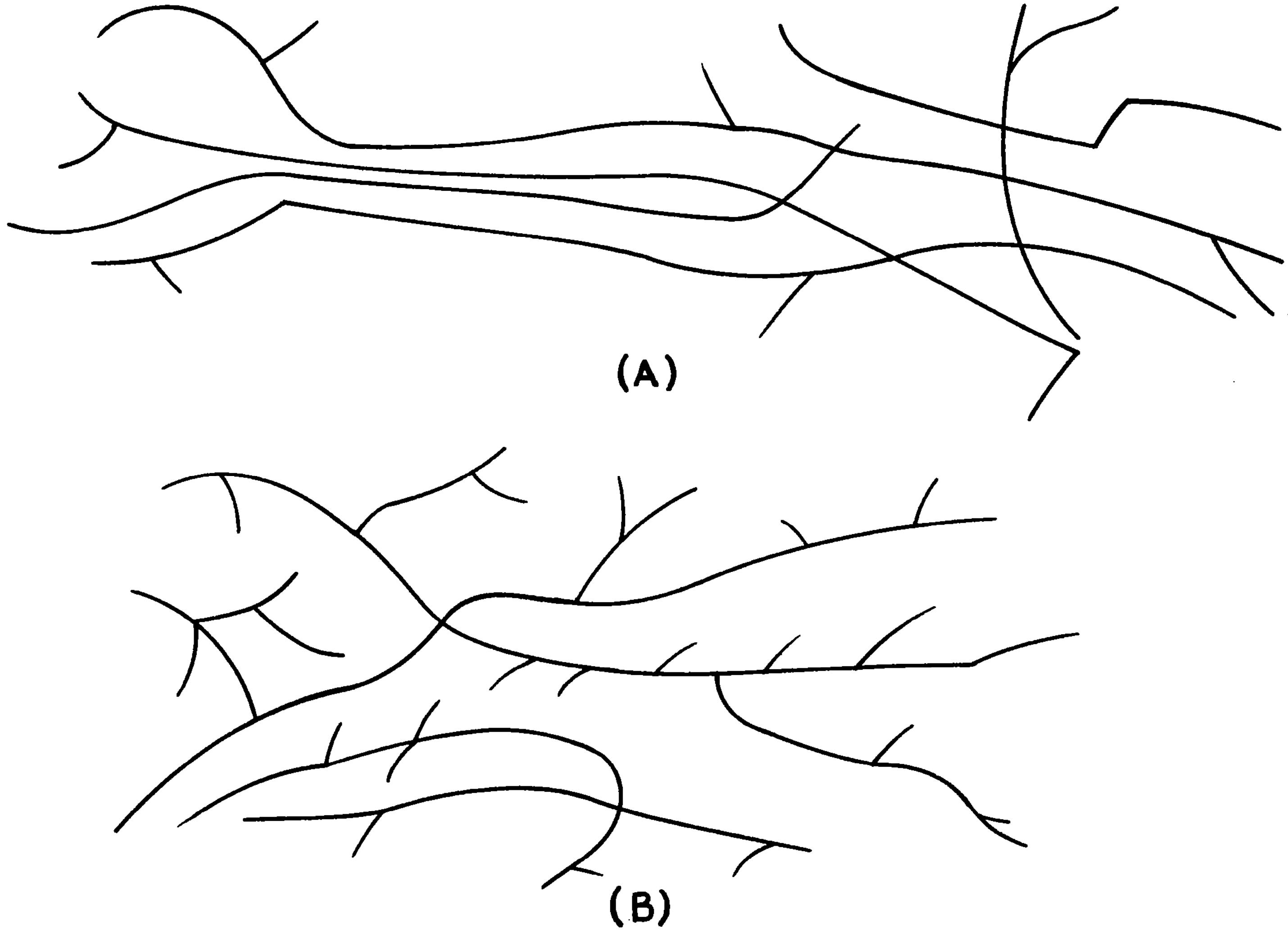
These IR scans do not show any unusual phenomena to have occurred in the extrusion of the UTG film. Data from the IR scan supports the conclusions drawn below on chain branching.

The three experimental DEX resins used in this research had the following characteristics. The average molecular weight (M_n) was approximately $M_n = 28,000$. The melt index of the resin, which was closely controlled in manufacture, was 5.8, 6.0 and 8.0. The density of the three DEX resins was: .9220, .9235 and .9250. Density, which is primarily a measure of the crystallinity of the polymer, is inversely related to the amount of short chain branching. Normally, the short chain branching is determined by IR scan and is equal to the number of short chain branches per 100 carbon atoms. The reason for the dependence of crystallinity on short-chain branching is that crystalline regions can be formed only from chain segments containing no interruption due to branch points (see attached figure). The more branch points there are, the fewer the crystalline regions that can be formed. Since the crystalline regions have a higher density than the non-crystalline or amorphous regions, the density of an actual sample is determined by the weight ratio of crystalline to amorphous material.

The extent of branching varies with polymerization conditions and with molecular weight; in low density polyethylenes there are 20 to 30 methyl groups per 1,000 carbon atoms and, therefore, since the average number of carbon atoms per molecule is around 2,000, there are 40 to 60 chain ends per molecule; there are evidently branch points at average intervals of 30 to 50 carbon atoms. In low density polyethylenes it appears that most of the branches are short, with between two to six carbon atoms; there are also a few long branches.

Long-chain branching is more difficult to measure. These measurements are based on the effect that long-chain branching has on the solution viscosity of a linear polyethylene with that of a branched polymer with the same value of the weight average molecular weight (M_w). From the ratio of these solution viscosity measurements, a long-chain branching index can be calculated. An approximate value for the number of long-chain branches per 100 carbon atoms for the resins used in this project is .02.

The amount of long-chain branching affects the breadth of the molecular weight distribution (MWD) as measured by the ratio of M_w/M_n, since the molecules containing these long-chain branches, which have substantially higher molecule weights, contribute more to M_w than to M_n and thereby increase the M_w/M_n ratio appreciably. MWD has an important effect on physical properties of the extruded film; specifically, properties involving large deformations, such as ultimate strength and the behavior of the melts, are particularly sensitive to molecular weight, to long-chain branching and



(A) FEW BRANCHES, HIGH CRYSTALLINITY (B) MANY BRANCHES, LOW CRYSTALLINITY

RELATIONSHIP OF BRANCHING AND CRYSTALLINITY
OF POLYETHYLENE MOLECULES

to the closely related parameter of MWD. The M_w/M_n ratio for the DEX resins was approximately 8, which is low, thus the MWD is narrow.

According to reference (a), the average length of polyethylene molecules, with the above branching characteristics and $M_n = 28,000$, is approximately 500 Å.

Although this is certainly variable, for example references (b) and (c) discuss polyethylene chain lengths of 10, 000 Å to 100, 000 Å, 500 Å appears to be a reasonable average molecular length for film produced from this resin. Using this figure, a commercial film of approximately 1/3 mil gauge, with a thickness of 76, 230 Å, has a ratio of film thickness to the average molecular chain length, R_t, equal to 152. 4. One of the films extruded in this program had a film gauge of 15, 500 Å, and this gives an $R_t = 31$. This is an improvement in the function R_t by a factor of about 5 over the best commercial film extruded heretofore.

The molecules across the thickness of the film frequently double back and intertwine with adjacent molecules. Orientation, of course, tends to align the molecules in the direction of the "working". If we assume a molecular film thickness of between 500 Å and 1000 Å, i. e., one to two molecules thick, as being the fewest number of molecules that are possible to achieve in a film, then a multiple of this would be a lower limit for a theoretical film gauge. This assumes the molecule is either oriented perpendicularly to the film or has long chain branches across the film thickness.

Arbitrarily, an order of magnitude, or a factor of 10, is selected as being reasonable for the number of molecules across the film. Therefore, the theoretically lowest limit in extruding films appears to be 5, 000 Å to 10, 000 Å or an R_t between 10 and 20.

Thus the practical limitation to extruding thin films, from the theoretical point of view of molecular chain length and molecular chain branching, appears to be approximately a gauge equivalency between 5000 Å (1.92×10^{-5} inch or 1/52 mil) and 10, 000 Å (3.85×10^{-5} inch or 1/26 mil); this is the theoretical lower limit for ultra thin film extrusion. However, as discussed below, mechanical properties and extrusion methods become overriding before this theoretically attainable gauge could ever be realized.

Film Thickness/Layflat Width

Achieving thin gauge film concurrently with good layflat width are not fully compatible objectives. Both depend on the strength and orientation of the film which enables the film to be drawn down. Several complicated and interrelated operations govern achievable ratios of film gauge to layflat width, as discussed below.

There is little doubt that orientation is the major factor controlling the mechanical properties of the film, and thus the ability to draw down to thin gauges and blow up to wide layflats. There are three sources of stress which may impose orientation during blown film formation:

(a) the shear stress causing flow of the visco-elastic melt through the die; this would normally result in swelling or melt elastic recovery of a subsequently unrestrained melt and any orientation imposed will be in the machine or longitudinal direction, and vary from zero at the center to maximum at the edges of the melt;

(b) the transverse or circumferential stress arising from the blowing process after the melt has left the die; this depends upon the air pressure within the bubble and the diameter of the bubble and, any orientation it imposes, is in the transverse direction,

(c) the stress applied by the nip rolls during the longitudinal or machine direction drawing process.

At the same time, molecular relaxation occurs continuously throughout the bubble forming and blowing process at a rate depending upon the temperature gradient of the melt from the die to the freeze line. Orientation arising in the die is small compared with that from melt drawing and does not directly influence the orientation finally frozen into the film; its importance lies in that it may affect the way in which the melt draws.

The main criteria affecting the mechanical properties of tubular film are therefore not only the relative magnitude of the transverse and machine direction drawing between the die and the freeze line but also the order in which they occur. This is not altogether surprising because the relaxation times of the molten polyethylene are comparatively short. The most likely orientation to be frozen and retained in the film, as well as the consequential crystallization behavior, are determined by the orientation existing in the melt at or just before the freeze line.

For a given die, the maximum layflat width possible to achieve is a direct function of the bubble blow up ratio (BR). BR is defined as the bubble circumference divided by the die-orifice circumference, or:

$$BR = \frac{2 \times FW}{\pi D} \quad \text{where } FW = \text{layflat width}$$

Practically, blowup ratio is a dependent function of output rate, freeze line distance and internal air pressure; in turn, these depend on several interconnected variables such as nip roller speed, and cooling air velocity, distribution and vertical location.

Normally, extruders are operated with a BR between 1.5 and 6.0 with 2.5 to 3.0 a common ratio. BR determines many of the transverse properties of the extruded film.

Draw-down ratio (DR) is similar to BR in that it determines many of the properties of the film, except these are primarily in the machine direction.

In the blown tubular process, using the normal blowup ratios of between 1.5 and 3.0, a large draw down in the machine direction is required. For example, film 0.0015 in. thick, made at a blowup ratio of 2:1 from a die with an annular gap of 0.030 in., will be drawn down in the machine direction in the ratio

$$DR = \frac{\text{die gap}}{\text{film thickness x BR}} = \frac{0.030}{0.0015 \times 2} = 10:1$$

compared with the 2:1 ratio in the transverse direction. It therefore appears that machine direction drawing, and consequently machine orientation, will predominate in any normal blown film process.

The blowup ratio used in the most successful UTG film extruded in this project was 2.55:1, which was quite average. (The BR range varied from 1.8 to 3.2). However, a maximum BR was not attempted during this first effort since thin gauge was of prime importance.

As shown above, standard commercial practice uses a draw down ratio of approximately 10:1. However, for the thinnest gauge film extruded in this program the DR was considerably larger.

$$DR = \frac{.017}{6.1 \times 10^{-5} \times 2.55} = 109.29$$

This is a factor of 10 greater DR than used commercially, or probably ever produced in any laboratory. Being able to match a resin and extruder output to achieve such a draw ratio is a significant result of this project. However, as discussed further below under Extruder Operation, mechanical problems were controlling aspects of the extrusion process.

DEVELOPMENT PHASE

General

The primary effort in this program was to extrude UTG films, and test these films. Some effort was devoted to alternate methods of providing UTG films, one being tentering.

Examining the extruder task first, all film extrusion can be classified as a "gentle art", and poor control of small details can result not only in an inferior product, but in the extreme, even in damaged equipment. Since this is true for commercial extrusion, steps in producing UTG films are extremely demanding.

Each production element in producing UTG films must be carefully controlled - from preparing the resin, cleaning the extruder die and air ring to lining the tower. Following this pre-start-up effort,during extruder operation, time and temperature control must be monitored continually. When each of these steps are matched to the overall production flow, excellent quality film can result. However inattention to one detail can produce a frustrating series of bubble blowouts; the attendant one-hour start-ups, before achieving thin gauges on the way down to try again for ultra thin gauges, can be costly in both equipment and man hours.

Production Flow

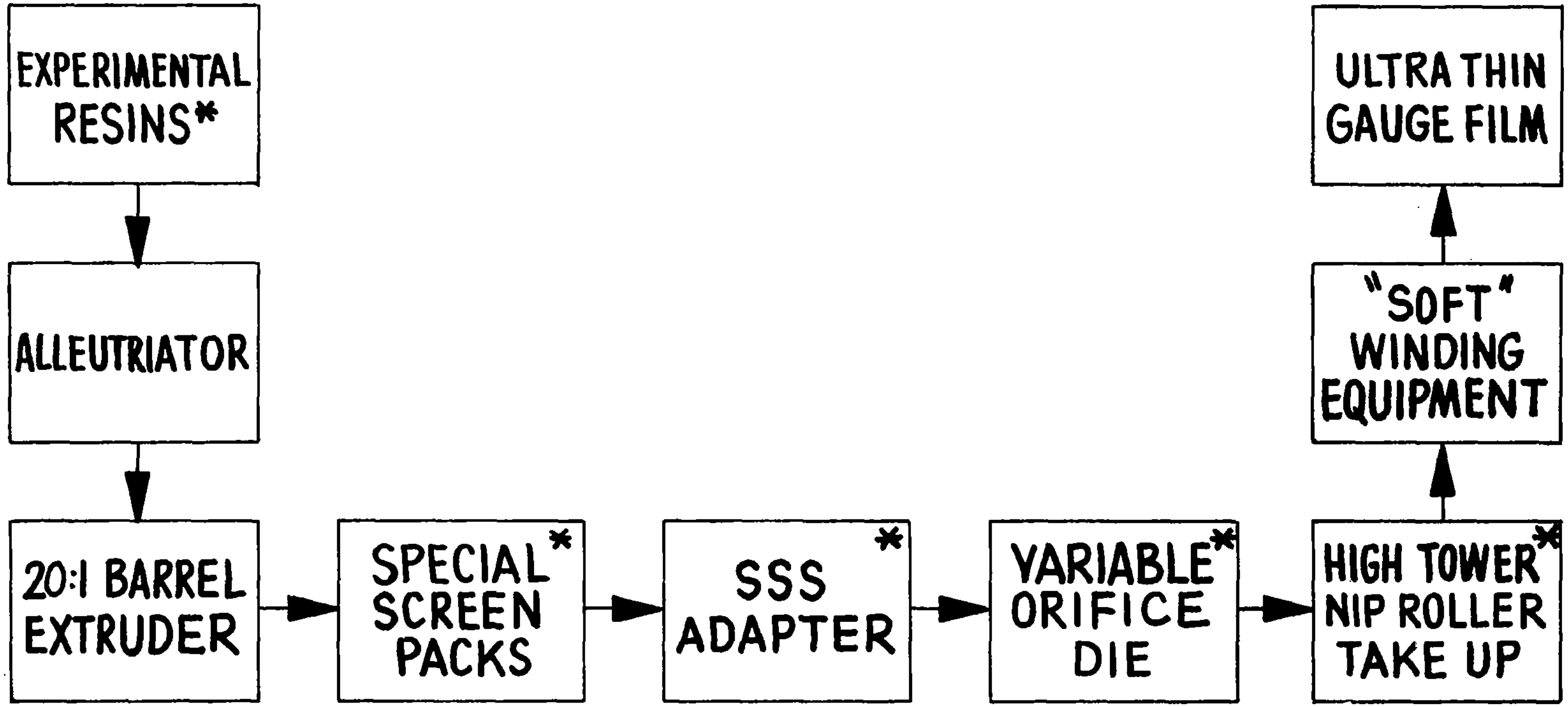
Producing blown tubular polyethylene film requires expensive equipment in a production facility. For this project, the following was required:

1. Experimental Resins
2. SSS Alleutriator
3. 20:1 Extruder
4. Special Screen Packs
5. SSS Adapter
6. SSS Special Die
7. High Tower, Nip Roller Take-up
8. "Soft" Winding System

Attached are both a production flow diagram that shows the sequence of operation and a schematic of a typical extruder system set-up.

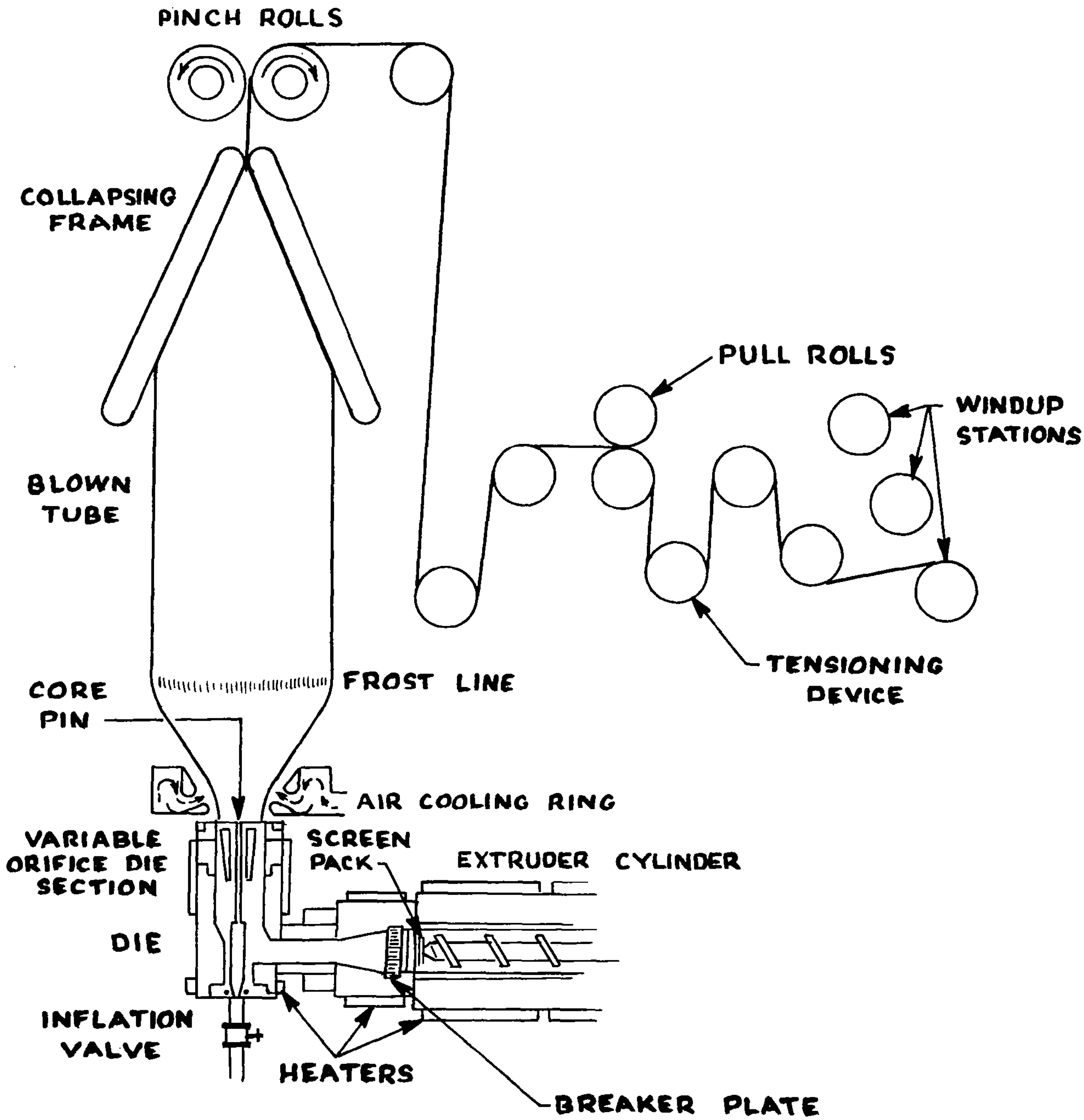
Resin

Experimental low density polyethylene resins for this program were provided by Union Carbide Corporation. The resins had the below tabulated physical properties. In addition, the quality control employed in production was much superior to normal commercial grade resin. For example, melt



*NON-STANDARD EQUIPMENT/MATERIALS

ULTRA THIN GAUGE
PRODUCTION FLOW DIAGRAM



UTG FILM EXTRUDER SCHEMATIC

index was controlled to ± .25 vice the normal ± 1.0 to 1.5 for commercial resin. The quantities tabulated below were determined precisely for each lot.

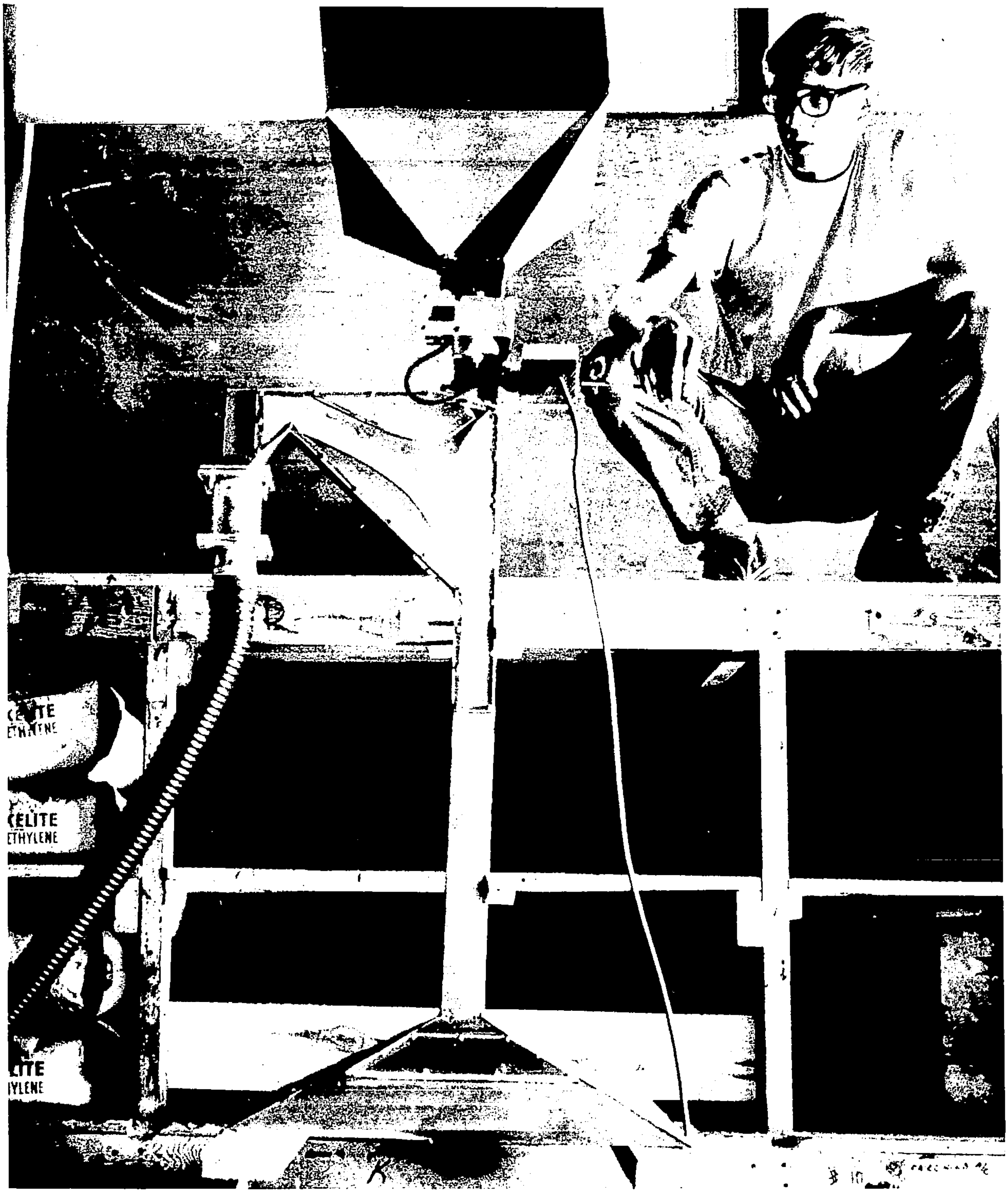
Resin Designation	Melt Index	Density	MI/ρ	Anti-Oxidant
DEX 8025	7.9	.9243	8.457	50 PPM BHT
DEX 8026	6.4	.9263	6.909	50 PPM BHT
DEX 8028	5.8	.9220	6.291	None
SSS Standard	5.0-6.0	.9218	5.424 to 6.509 (av. 5.967)	AR

The objective in the DEX resins was to increase the density over the SSS Standard as well as provide a range of Melt Indices for evaluation. The anti-oxidant added was butylated hydroxytolune (BHT) and was expected to reduce gels and fisheyes from forming in the film. Control of both spherelites in the film and the cross-linking polymerization of the molecules is achieved through the use of higher melt index/density resins, thereby theoretically enhancing the capability for extruding UTG films.

Equipment Recommendations

Alleutriator. The SSS reverse blow, air bath alleutriator cleans the resin effectively prior to entering the extruder hopper. The alleutriator design is based on balancing the pull of gravity on the resin by the flow of wash air, wherein the lighter weight "fines" and "extruder dirt" are washed out a side port. The entire wash section and collector hopper are visible through a plastic lucite plate.

The throat section requires a smooth, laminar like flow to achieve satisfactory separation and prevent "dirt pockets" from forming. Although the resin is cleaned at the factory prior to shipment, any transportation or vibration appears to cause the resin to develop "fines" and/or dislodge particles from the basic resin pellets. These impurities must be cleaned out of the resin. The high "area to volume" ratio of the impurities produce unequal temperature distribution throughout the resin melt as well as an uneven pressure distribution in the die. Both of these results can cause "fisheyes" and "gels" to form in the film and "blowouts" will occur frequently, an unacceptable condition when extruding UTG film. Attached is a photograph of the SSS Alleutriator.



SSS Alleutriator

Extruder and Ancillary Equipment. Two extruders were used for this program.

(1) Modern Plastics Machinery Extruder: 3-1/2 in. diameter barrel; 15:1 length to diameter ratio.

(2) Gloucester Engineering Company (GEC) Extruder: 2-1/2 in. diameter barrel; 20:1 length to diameter ratio.

The Gloucester unit was most successful in the effort to produce UTG film and it, or similar high quality equipment, is recommended. The GEC extruder was electrically heated, with a 20 HP eddy current drive with reduction to result in 140 - 150 maximum screw rpm. The extruder had 3 heating zones, total rating 15 - 18 KW on the barrel. No cooling water was used.

Whenever this gauge tubular film is to be extruded, the following general equipment specifications are recommended:

a) Extruder Base - Heavy duty base of welded, reinforced steel or casting so that proper alignment of all of the extruder components is assured and with a minimum of vibration. All of the mounting surfaces of the base for the gear reducer, etc., should be machined. A low boy extruder base is recommended, particularly if getting the tower height recommended is a problem. (See attached photograph).

b) Power Reduction - Either an electrical vari-speed drive for small extruders or a herringbone type gear reducer with internal lubrication system, rated for at least 1.25 x HP drive motor for larger units are recommended.

c) Thrust Bearing - Self-aligning spherical roller bearing with internal lubrication system, rated for B-10 life 50,000 hours at 10,000 psi at 140 - 150 rpm.

d) Drive - Ample horsepower for the installation with the necessary belts, guards and motor starter.

e) Barrel and Head Section - The barrel should be one piece heavy wall steel with a centrifugally cast X-alloy liner; provide at least 3 heating zones with either resistance or induction type heaters, and have the necessary thermocouples and wiring to connect barrel to instrument panel.

A bourdon type pressure gauge 0 - 10,000 psi is advisable and should be located at the end of the barrel between the tip of the screw and

Gloucester Engineering Company
Thermoplastic Extruder Used in SSS Tests

the breaker plate. The barrel cover should be rated for 10,000 psi and sealed on the flat surfaces of the breaker plate and be equipped with necessary heater and thermocouple.

f) Feed Throat and Hopper - The feed throat should be a heavy duty casting and have a large opening to the feed screw. The mounting surfaces of the throat to the thrust housing and barrel should be machined.

The hopper should be provided with a sight glass to show resin level and provisions for easily emptying the hopper without removing from the extruder.

g) Feed Screw - A recommended screw for this application is a polyethylene type screw of SAE 4140 molybdenum chrome steel, polished flame hardened flights. Extruder screw engineering is a major "black-art" area in film extrusion.

h) Instrument Panel - Provide 6 temperature controllers, 3 for the barrel and 3 for the die. The type of controller will depend on the barrel cooling system and can be either 3 position with on/off cooling or 2 position of the on/off proportioning type. The controllers for the head section and die should be a proportioning on/off type.

The controllers for the die can also be located on another panel closer to the die; this panel should include a screw rpm indicator, drive motor ammeter or wattmeter. It is recommended that the panel with these instruments be located so that the operator at the controls can see the necessary instrument readings without moving from the control station.

The main panel should contain all of the necessary wiring, contactors, fuse blocks, etc., to link the various components and to protect the equipment. (Most of the panels being supplied today are prewired in accordance to Joint Industry Commission Standards and are recommended).

Adapter and Screen Pack. The internal surface of the adapter coming in contact with the resin should be polished and hard chrome plated. A clean screen pack and breaker plate are mandatory. Replacement of screen packs on a routine basis is recommended.

Die. The die is a key element for successful extrusion of thin film. Dies used in blown tubular film extrusion are fixed orifice with a die gap of .025 to .040 inch; however, a variable orifice die is mandatory for UTG extrusion. Die gap was an important, but not completely definitized variable in the extrusion process, as is discussed in detail below. (See attached photograph).

As discussed below, an improved die requirement became evident in the first UTG extrusion operation. Aerodynamic bubble instability became such a problem that external stabilization was necessary. The instability commenced from the non-tangential air entry from the air blowers below the frost line up through initial contact with the stabilizing bars in the tower. This problem was strictly associated with the thin film not having sufficient "body". From this requirement, the double-orifice die originated. (See attached drawings).

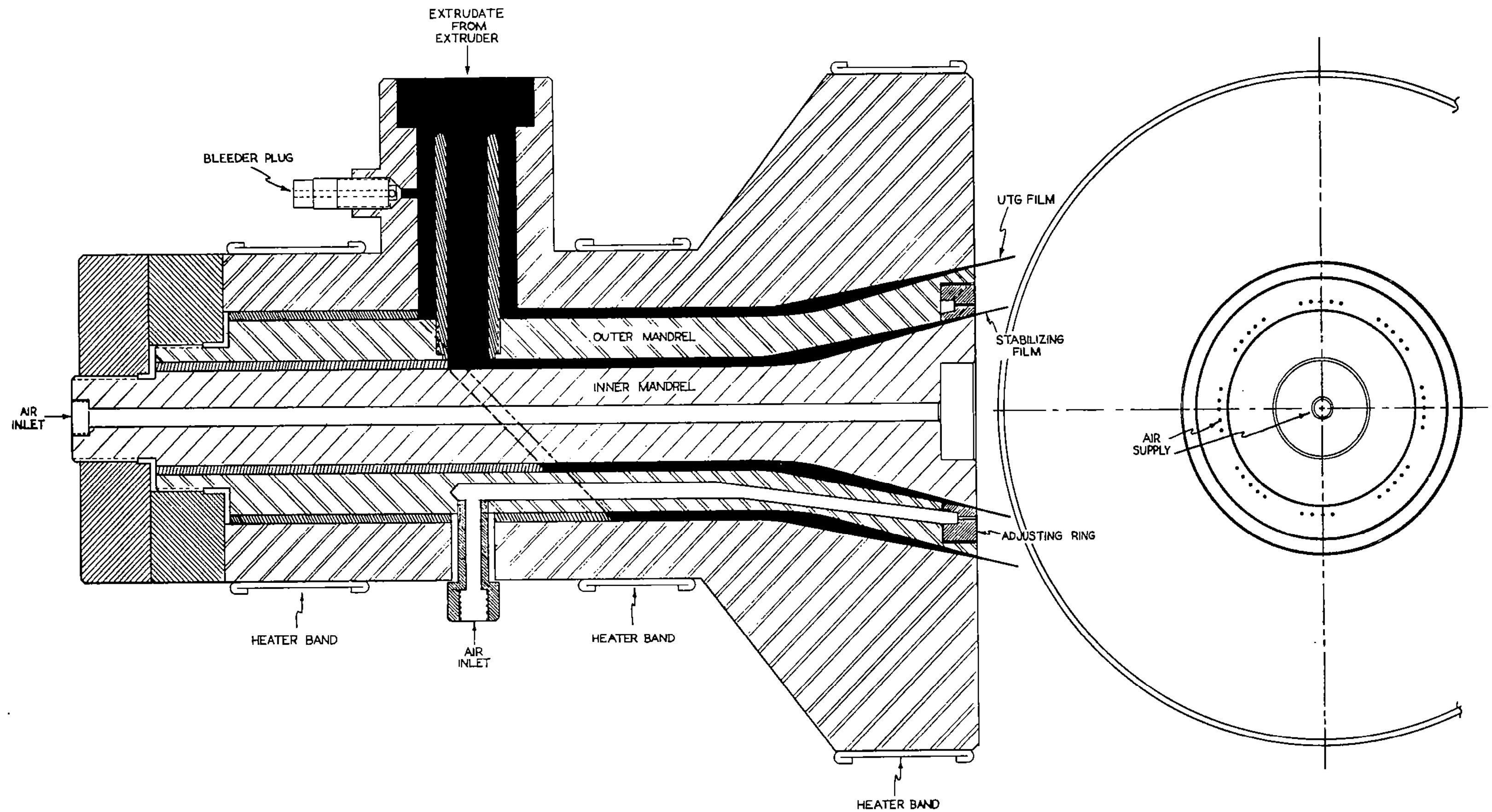
The double orifice die is designed to extrude two concentric rings of tubular film, the inner being heavy gauge and the outer thin gauge. (The die can also be adjusted for single film extrusion).

Other features of this die are:

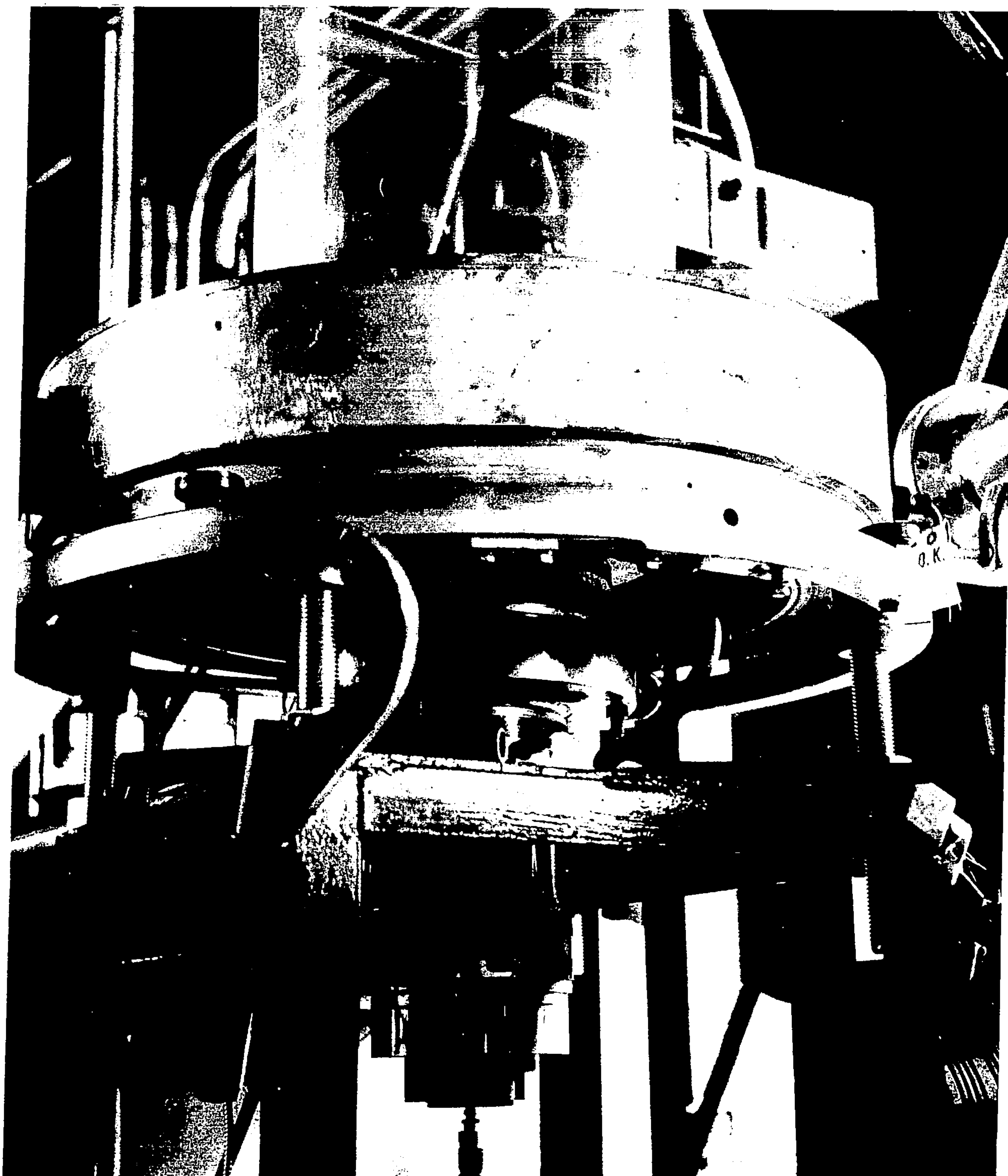
1) Uniform flow channel.
2) Specially designed spider to provide streamline melt flow cavitation.
3) Flexibility in setting die gaps.
4) Uniform heat distribution through use of induction heat in manufacture.
5) High control facets with operating pressures from 2, 500 to 3, 500 psi.
6) Very precise steel die lips for close tolerance control.
7) Uniform air distribution around bubble through use of air rings. (See attached photograph).
8) Precise air direction and volume control.
9) Film layer, deblocking medium, injection ring.

Air Ring.. The air ring should provide a smooth non-tangential flow of air against the hot bubble. Controllers for the air ring should provide infinite control steps from zero to maximum output.

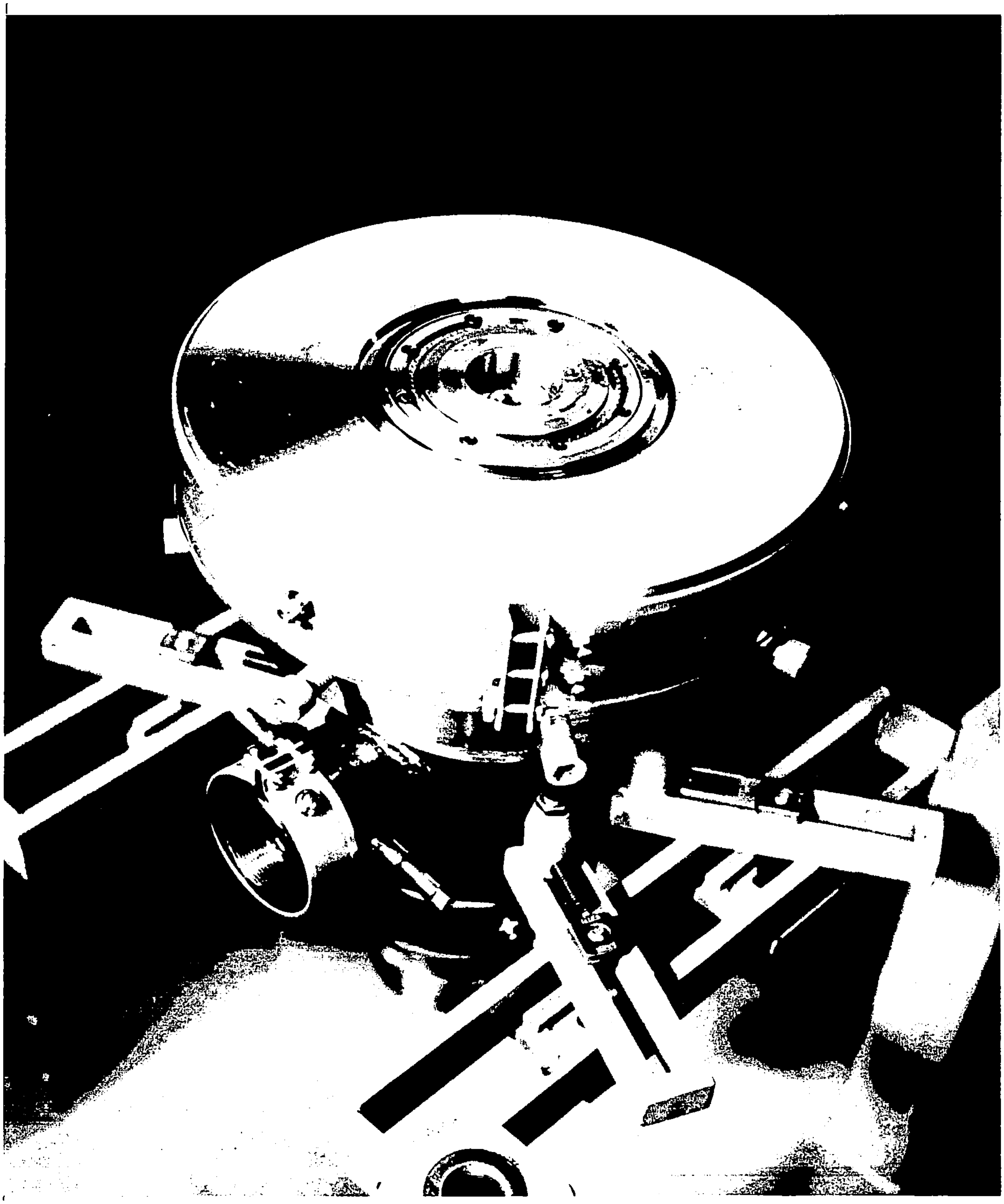
Cooling Air Blower. The recommended blower for this application should be rated at approximately 2, 000 cfm at 6 in. H_20 static pressure. In most instances, this will be an adequate supply for a double air ring installation. However, if the baffling in the air rings is unusually restrictive, it may not be sufficient. The displacement of a blower falls off rapidly as the back pressure goes above the static rating of the blower. Therefore, the supplier should be consulted as to back pressures and blower specifications for the rings being supplied. The air blower should be filtered to clean all dust and foreign particles from the air being ejected from the blower onto the films.



FUNCTIONAL SCHEMATIC DIAGRAM - DOUBLE ORIFICE DIE



6" Variable Orifice Die
Used by SSS in Tests



SSS Double Orifice Die
For UTG Film Extrusion

Tower Collapsing Frame and Nip Roll.

a) The recommended tower height for this application is a minimum of 25 ft, preferably 40 ft. Usual fabrication is of square tubular steel. A working platform around 3 sides of the tower of collapsing frame level is recommended. (See attached photograph).

b) Collapsing media recommended are hardwood slats 3 inches wide on 5 in. centers, sanded and polished on the surfaces contacting the film. These should be mounted on rigid metal frames that are fully adjustable at top and bottom.

c) The nip rolls should be driven by a 3/4 - 1 HP motor. A variable speed mechanical drive is preferred. The rolls should be at least 6 inches in diameter x 48 in. wide. One of these, the steel roll should be on fixed bearings. The rubber back-up roll should be mounted on air cylinders with provisions for controlling opening and closing of the nip and the pressure of this roll on the steel roll. The back-up roll should be steel covered with Neoprene 50 durometer hardness. The speed range of the nip rolls should be 10 - 300 fpm with 400 fpm desirable.

d) At the floor level at the base tower, the following operator controls and instruments are recommended: nip roll - stop/start and speed control; nip roll - pressure control and open/close control; nip roll - FPM gauge; bubble air supply control; extruder stop/start and speed control.

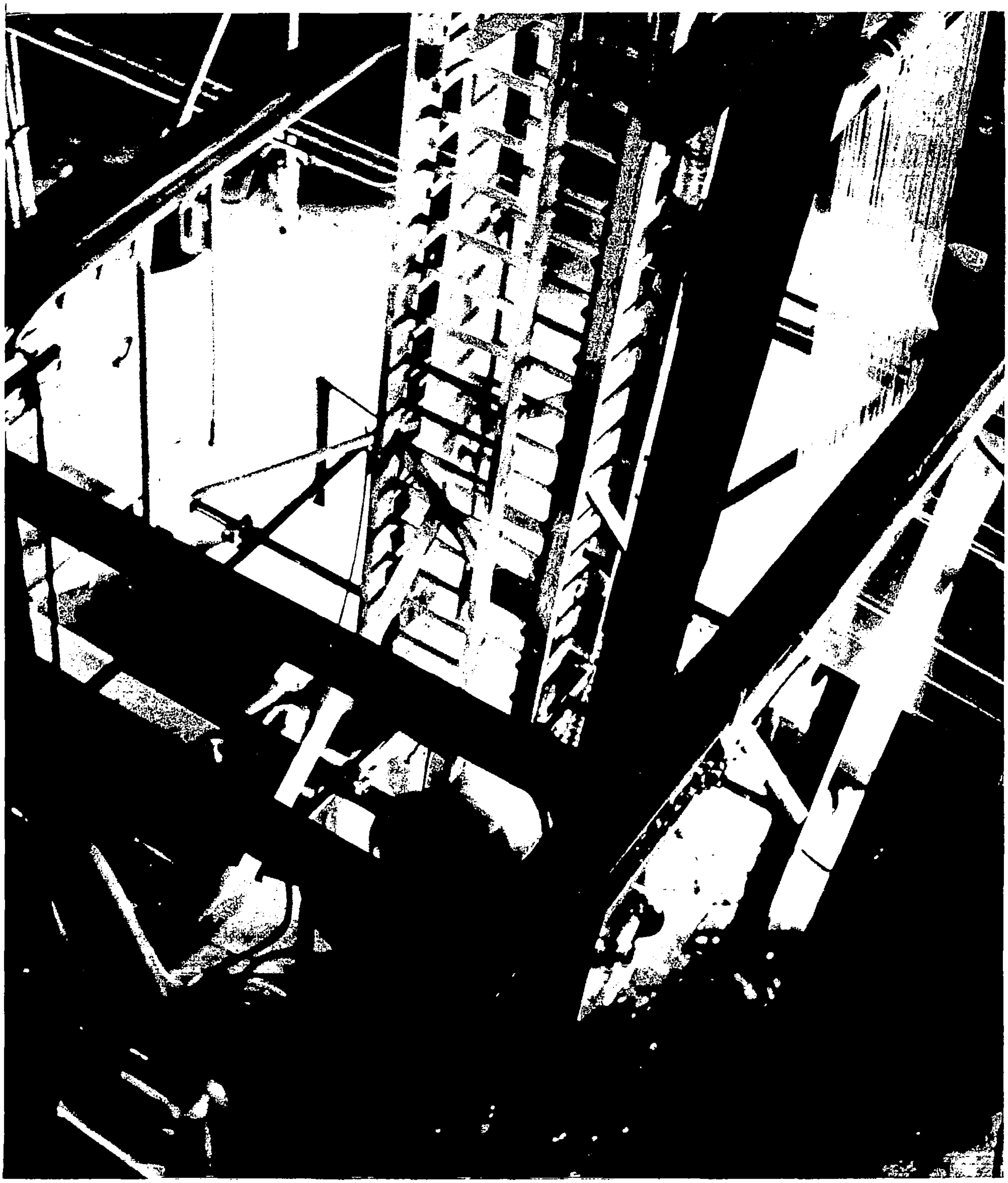
Idlers Pull Roll.

a) To guide the film from the nip rolls to the winding sections idler rolls 2" - 3" diameter x 64" wide-free turning, aligned and spaced about 36" apart are recommended.

b) To allow winding the film at the tension desired rather than at the high tensions necessary to pull the film from the nip rolls to the winder, a secondary nip or pull roll is recommended. These both should be Neoprene 50 "A" durometer and 4" - 5" diameter having the same speed range as the nip rolls atop the tower. A safety stop and quick roll opening device is recommended.

Wind-up.

Two roll turret wind-ups are recommended for this application. For the thin gauges under discussion, a 48 in. roll face winder would be adequate. Automatic film roll centering control and roll up tension control are mandatory.



High Tower Take Up System
Used for UTG Film Extrusion

Anti-Contamination. To keep foreign contamination to a minimum, a closed resin handling system is mandatory. In production, a completely enclosed tower and extruder section is also recommended.

Extruder Operating Techniques

As quoted and discussed above, operating an extruder is a "gentle art". Many "tricks of the trade" have evolved out of the tests conducted in this program. This section discusses the practical problems of operating the equipment described above to produce UTG film.

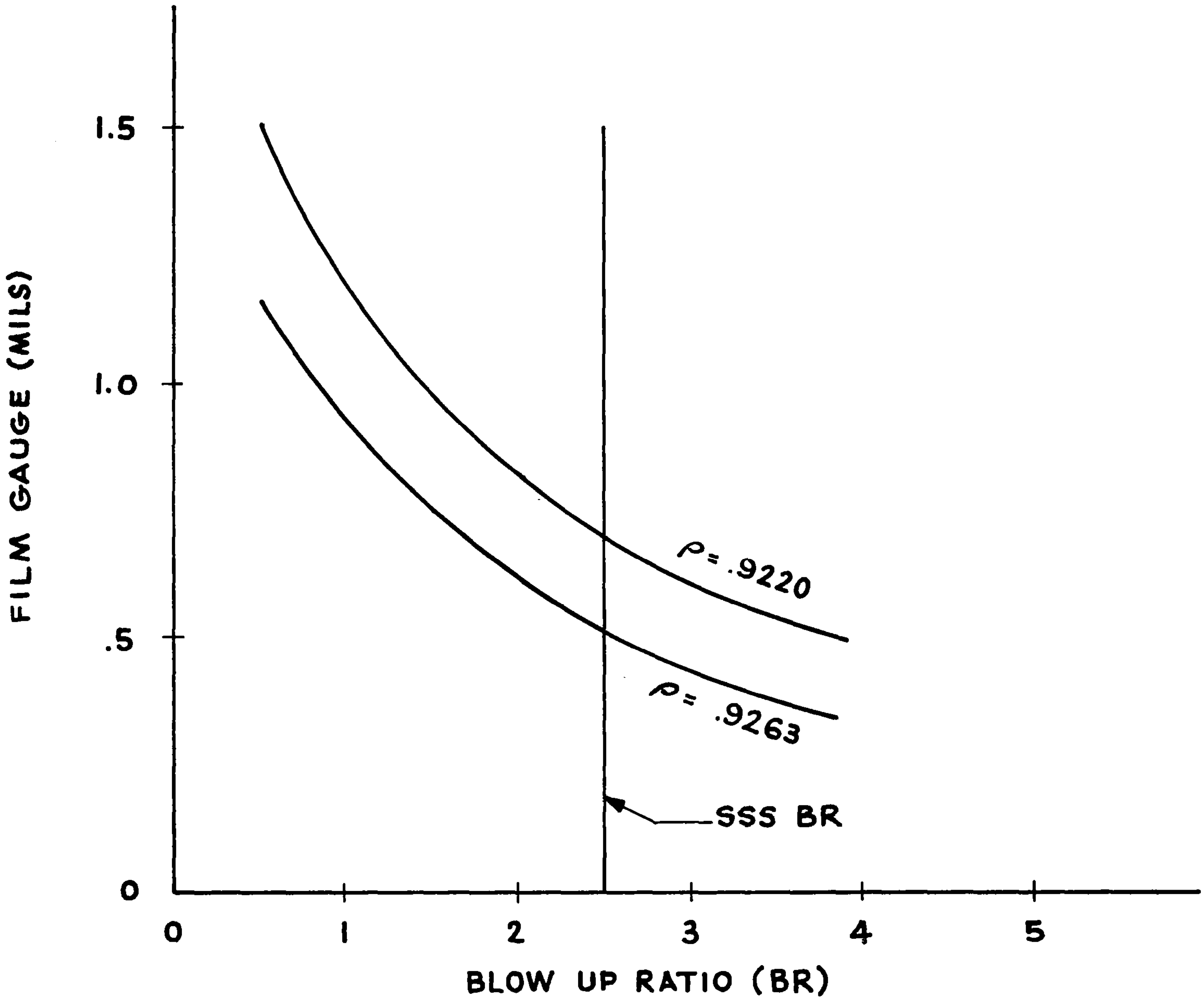
The "art" enters the UTG extrusion operation when the extrudate leaves the die. The melt should be slightly hotter than normal to provide good drawing characteristics. The frost line should be controlled by the relationship between the extruder drive speed, the nip roller take up, and the bubble size characteristics to provide about 18 in. FLD. Of course, the frost line should be completely symmetric in a horizontal plane, thereby verifying die centering.

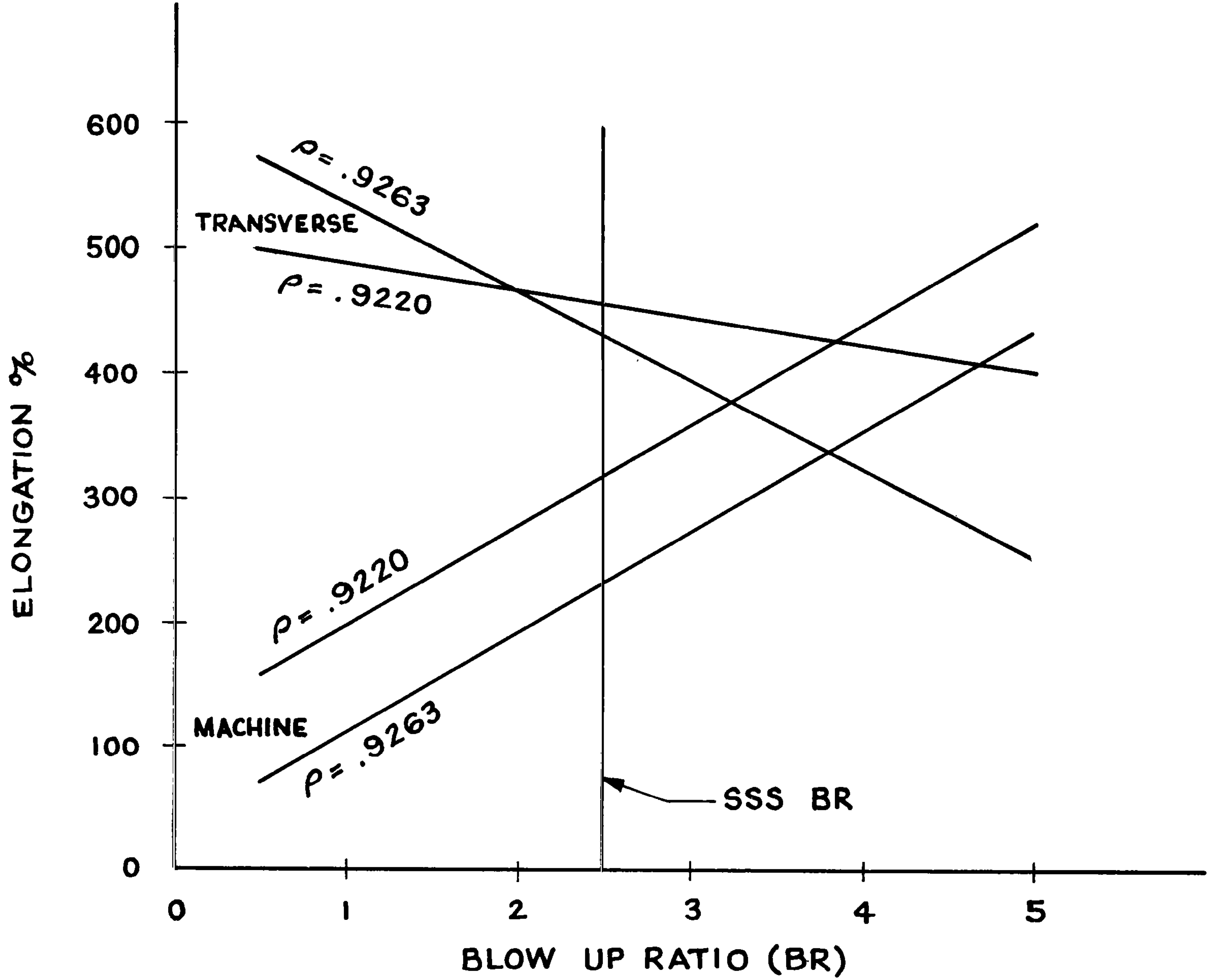
If the extruder was not perfectly clean, or if a resin with different characteristics had been used previously, the first six to ten hours of UTG extruder operation was a series of blow-outs until all the contaminants and polymerized bits of resin were completely flushed out. Of course, this mandatory requirement for cleanliness and quality extrusion operation has the beneficial result of extremely high quality, blemish clear film.

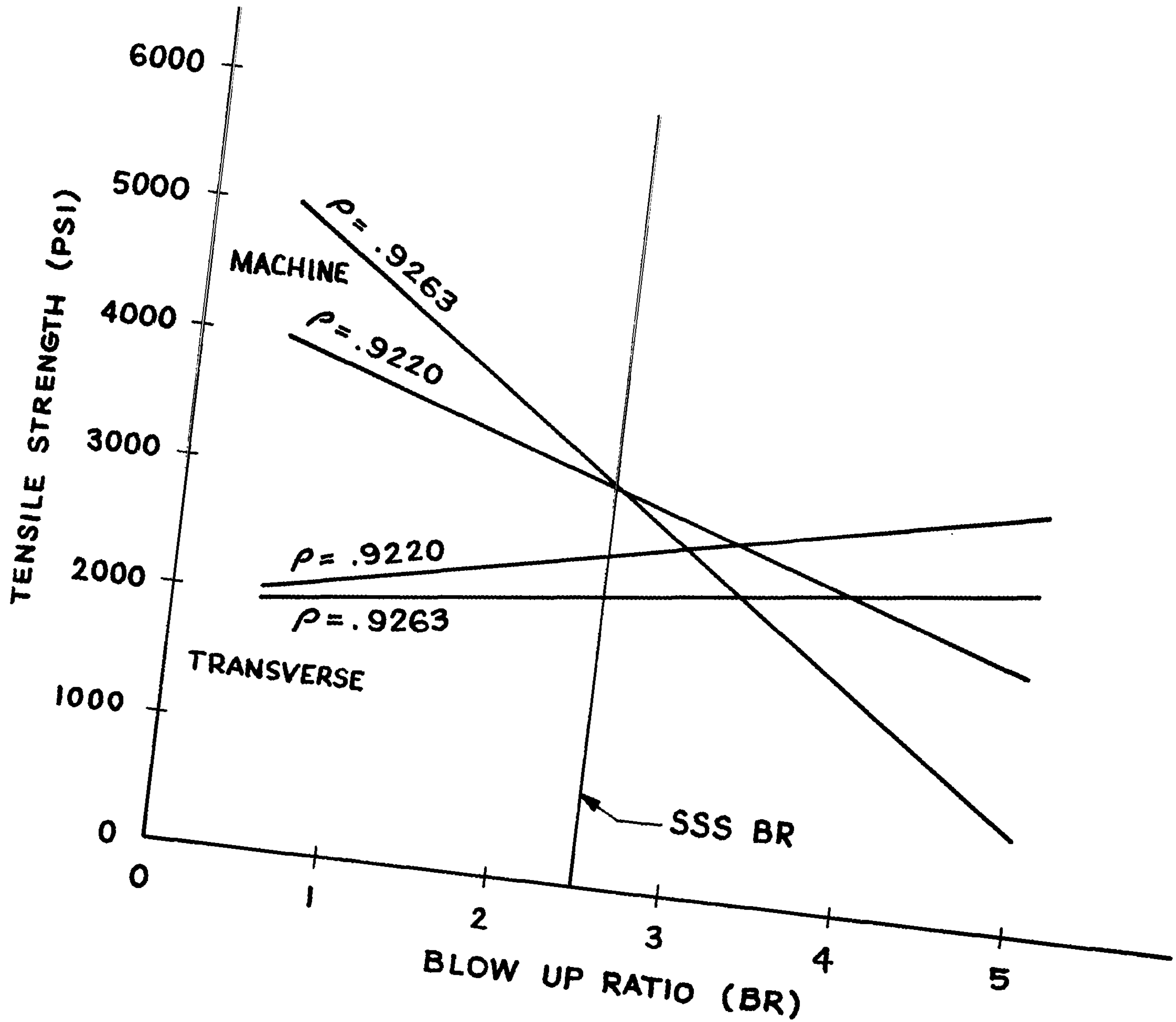
Another operating characteristic when extruding UTG film is that frequently the nip rollers are required to operate at maximum capacity. Consequently, the nip drive must have excellent control capability throughout its full operating range. Any variability in speed control, of course, would result in a blowout.

All UTG extruder control operations require very slow incremental changes to the extruder screw speed, the nip roller take up speed, and the air supply controlling bubble characteristics. Otherwise, normal machine operation techniques are used. However, it was found necessary at all times for an Engineer to direct the actual operation. This was mainly because the operator must not only understand all of the problems and potential solutions from the resin characteristics through extruder control techniques but also should understand the effect of extrusion variables on the fundamental properties of tubular polyethylene film. (See attached graphs).

The greatest problem encountered in extruding UTG films was bubble oscillation or "dutch roll". The bubble would execute an aerodynamic


FILM GAUGE (MILS)
1.5
1.0
.5
0
ρ= .9220
ρ= .9263
SSS BR
0
1
2
3
4
5
BLOW UP RATIO (BR)


ELONGATION %
600
500
400
300
200
100
0
0
1
2
3
4
5
BLOW UP RATIO (BR)
TRANSVERSE
ρ= .9263
ρ= .9220
MACHINE
ρ= .9220
ρ= .9263
SSS BR



TENSILE STRENGTH (PSI)
6000
5000
4000
3000
2000
1000
0
MACHINE
ρ= .9263
ρ= .9220
ρ= .9220
ρ= .9263
TRANSVERSE
SSS BR
0
1
2
3
4
5
BLOW UP RATIO (BR)

motion reminiscent of a "dutch roll". This motion on occassions would increase in magnitude to cause the bubble to either break or strike the side of the die/air ring and burn out. However, the surprising result was the amount of bubble oscillation what could be withstood by the extremely thin film before any failure would develop; this is either a consequence, or possibly a cause of the very high tensile strengths achieved in the film.

The solution to this problem was the double orifice die by which a stabilizing and supporting "heavy gauge" film will be extruded on an inner concentric ring to support the UTG film above the frost line, thereby alleviating this major extrusion problem.

To date the bubble was supported above the frost line by a conventional tower collapsing framework lined with paper. This scheme worked satisfactorily for the gauges produced but did not necessarily reduce below frost line oscillation; it is believed that any lower gauges, toward the goal of 1/20 mil, will require this improvement.

One installation refinement that can be helpful is related to air cooling. The bubble shape, and so the mechanical properties of the film produced, are affected significantly by the temperature gradient between the die and the frost line and therefore by the particular air cooling arrangements used. The beneficial effect that the air cooling system can have in modifying the bubble shape and producing film of higher impact strength is obtained by increasing the distance between the die and the point at which the cooling air stream strikes the molten bubble, and at the same time increasing the flow of air to maintain a constant freeze line distance. However, factors such as bubble stability, as discussed above, must also be considered in attempting to use this.

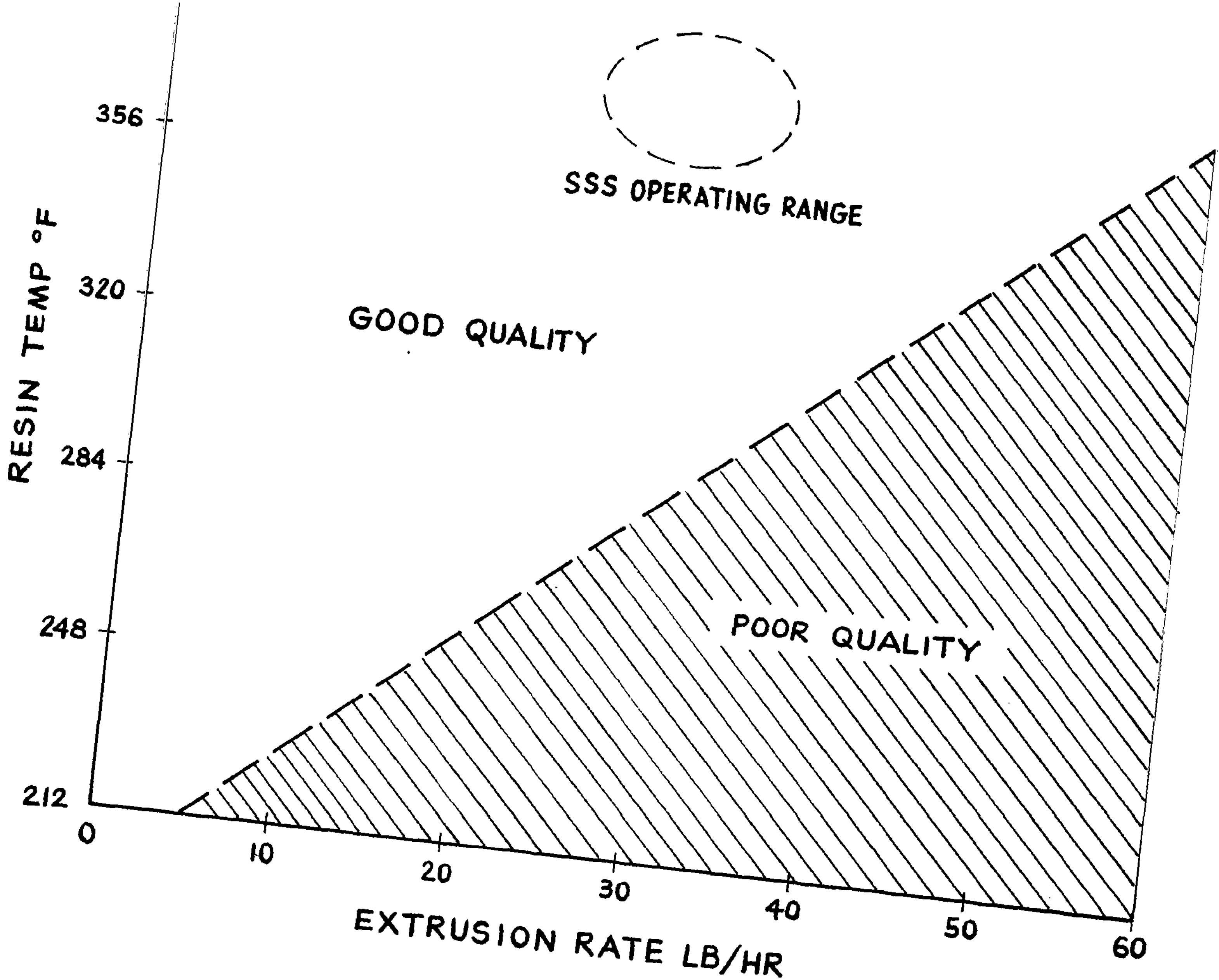
Three graphs follow which present the extruder operating area employed by Sea-Space.

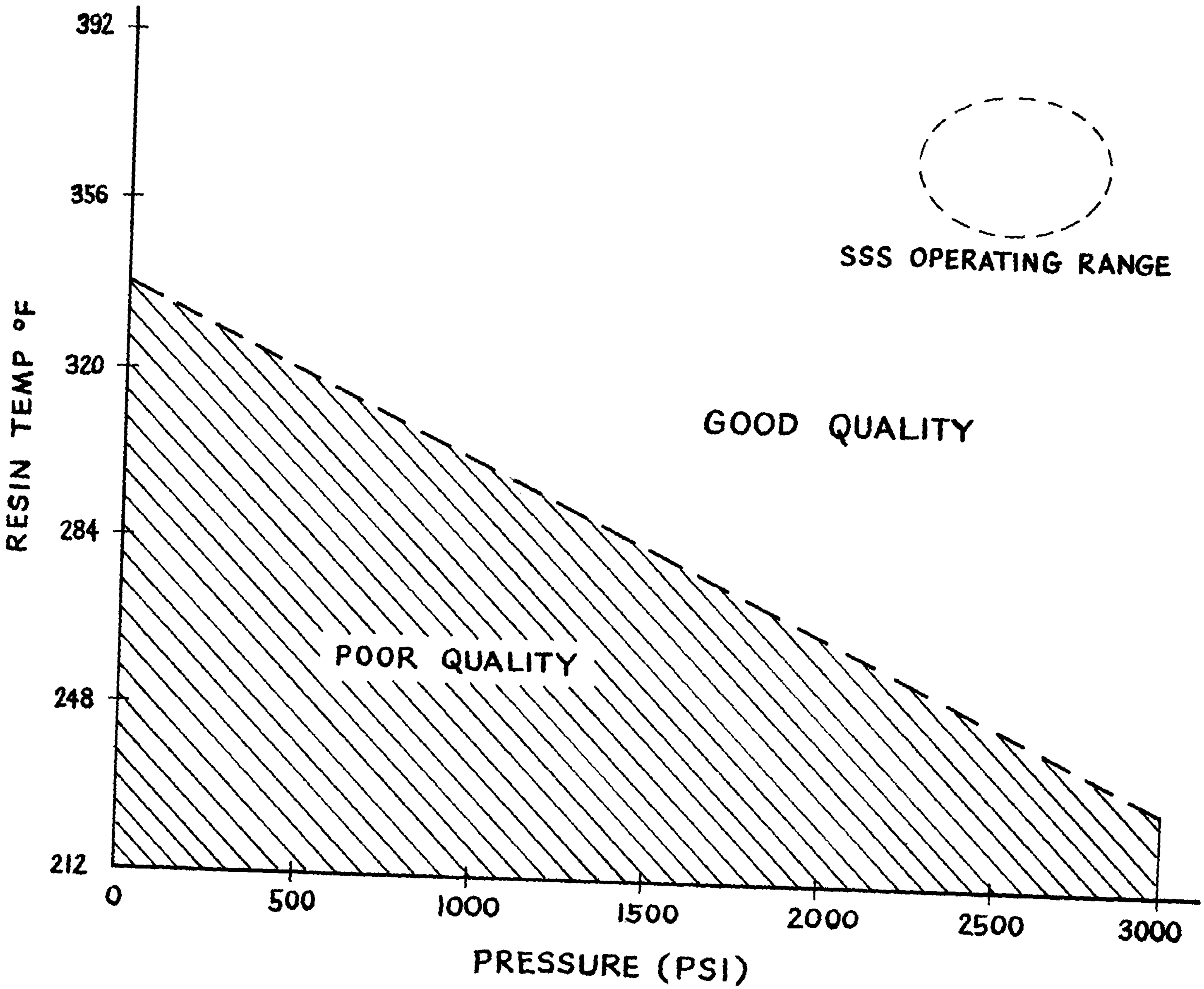
Extruder Operations

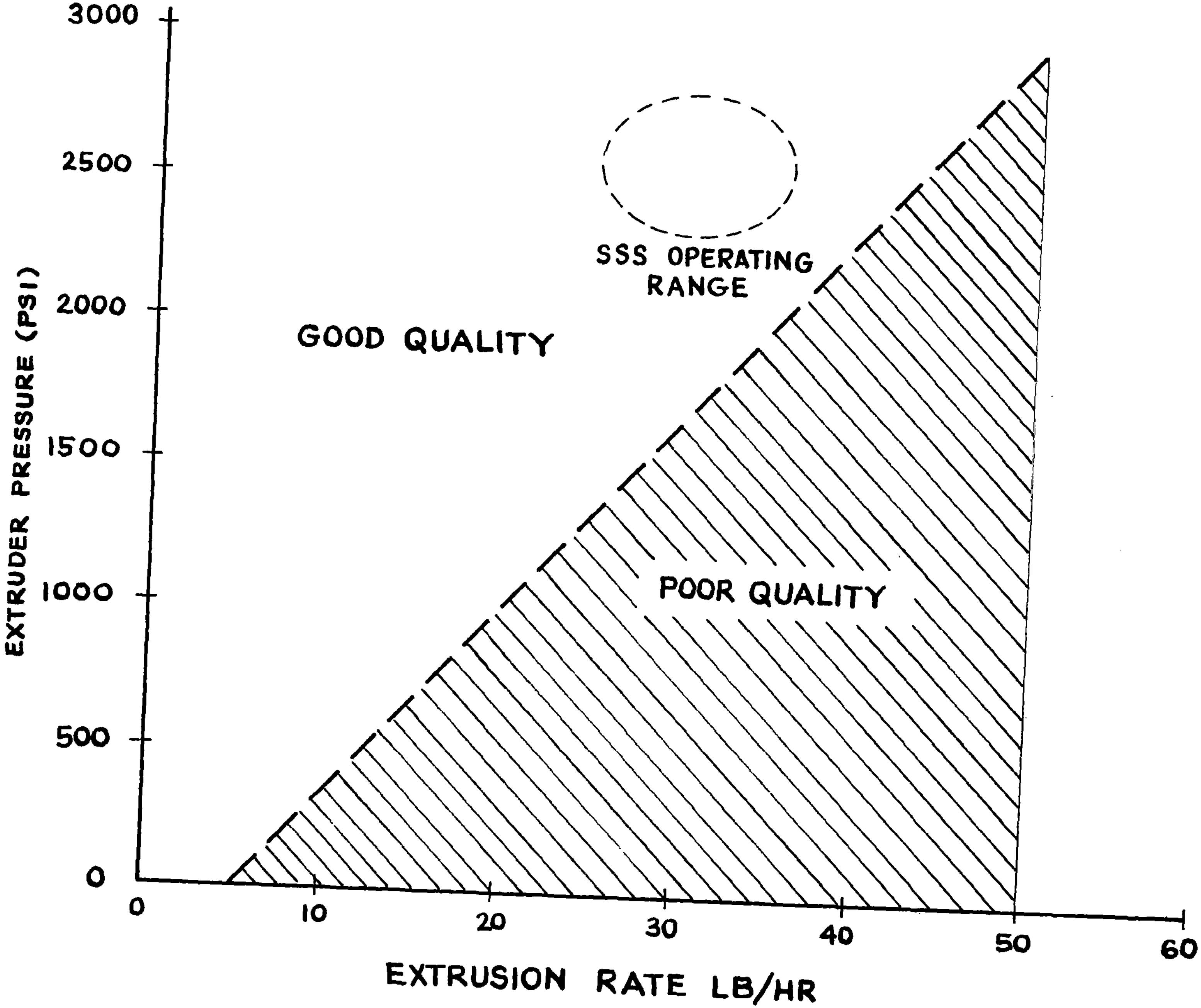
During this effort the following extruder operating periods were used in accomplishing the development Phase.

Date	Hours	Resin	Equipment
3/11/64	4-1/2	SSS Std	MPM 3-1/2"/FD
8/29/64	8	SSS Std	MPM 3-1/2"/VOD
12/3/64	16	SSS Std	GEC 2-1/2"/VOD
12/21/64	27	DEX	GEC 2-1/2"/VOD

FD = Fixed Die VOD = Variable Orifice Die LF = Layflat


SSS OPERATING RANGE
GOOD QUALITY
POOR QUALITY
RESIN TEMP °F
356
320
284
248
212
0
10
20
30
40
50
60
EXTRUSION RATE LB/HR


392
356
320
284
248
212
RESIN TEMP °F
SSS OPERATING RANGE
GOOD QUALITY
POOR QUALITY
0
500
1000
1500
2000
2500
3000
PRESSURE (PSI)


3000
2500
2000
1500
1000
500
0
EXTRUDER PRESSURE (PSI)
0
10
20
30
40
50
60
EXTRUSION RATE LB/HR
SSS OPERATING
RANGE
GOOD QUALITY
POOR QUALITY

Film Results

The following ultra thin gauge film was produced during this program:

Resin	Gauge (Mil)	Gauge (Inch)	Gauge (Micron)	Gauge (Å)
SSS Std	1/13.5	7.40×10^{-5}	1.88	18,796*
SSS Std	1/11.7	8.54×10^{-5}	2.17	21,691
SSS Std	1/9.5	10.5×10^{-5}	2.67	26,670
SSS Std	1/9.3	10.7×10^{-5}	2.72	27,178
SSS Std	1/9.3	10.7×10^{-5}	2.72	27,178
SSS Std	1/9.2	10.9×10^{-5}	2.77	27,686
DEX 8026	1/10.8	9.2×10^{-5}	2.34	23,368
DEX 8026	1/10.3	9.7×10^{-5}	2.46	24,638
DEX 8028	1/13.9	7.2×10^{-5}	1.83	18,288
DEX 8028	1/14.3	7.0×10^{-5}	1.78	17,780
DEX 8028	1/16.4	6.1×10^{-5}	1.55	15,494**
DEX 8025	1/14.9	6.7×10^{-5}	1.70	17,018
DEX 8025	1/15.2	6.6×10^{-5}	1.68	16,764
DEX 8025	1/15.4	6.5×10^{-5}	1.65	16,510***

* Best run with SSS Std.   **Best run with DEX   ***2nd best run with DEX

Note: Each significant run is recorded and not the many runs required to build up to that point.

Extruder Results

Although four resins were tested, a clear advantage of any one resin over the others was not obvious. The thinnest gauge film was extruded with DEX 8028. This resin had the lowest MI and density, and no anti-oxidant, and thus appears to be superior. However, UTG film was also achieved with the other three resins and it is not certain that the operator's learning curve was not responsible for the slightly better results of DEX 8028, which was the last resin run.

A summation of the resin evaluation thus must conclude that all resins were very good for UTG film production and DEX 8028 was superior.

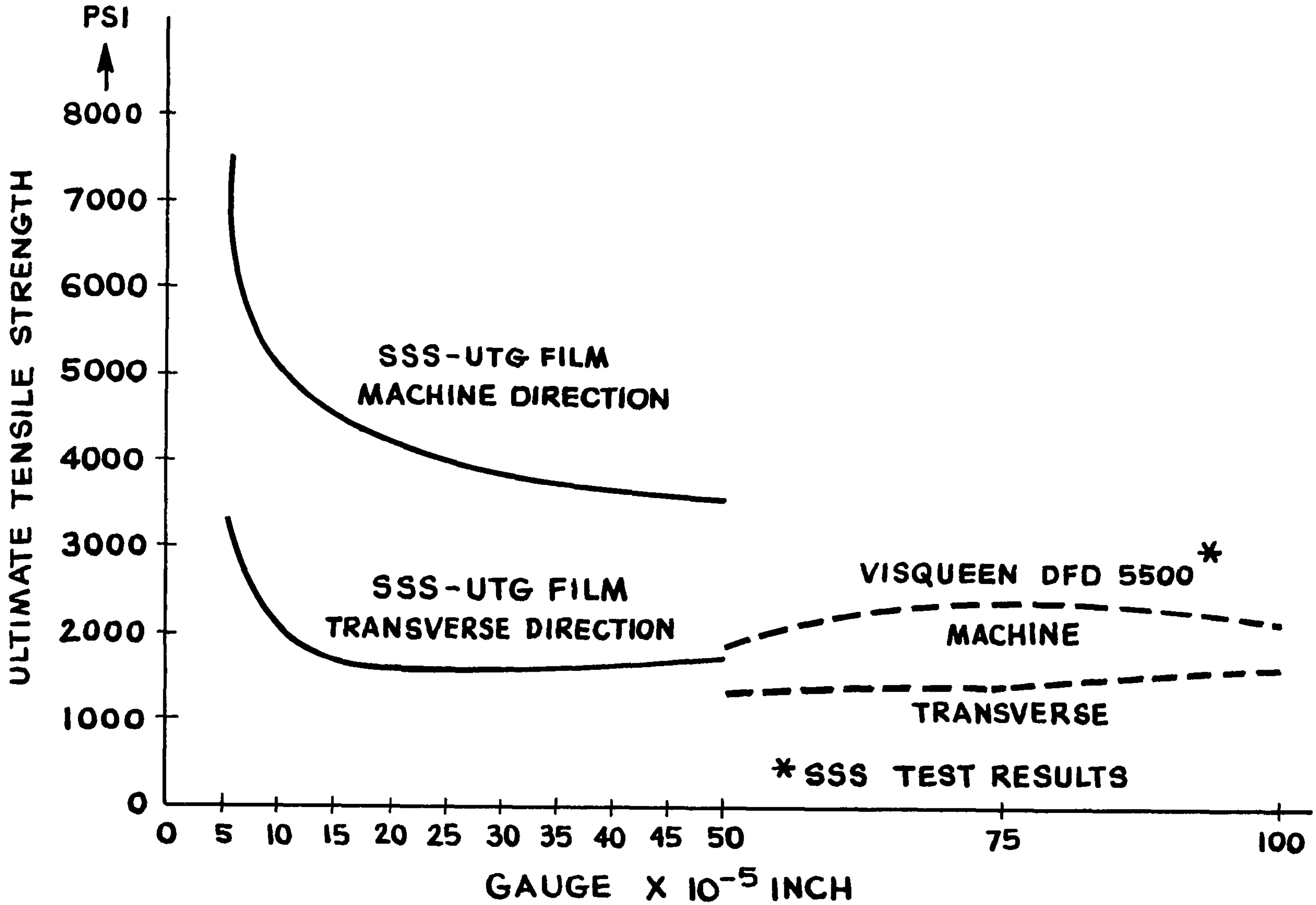
Similarly, no unequivocal advantage was demonstrated for the die gap to be used. Three die gaps were used: .011, .017 and .030 inch. The most successful results were achieved with a gap of .017 inch and this setting is recommended. The larger gap of .030 inch is not recommended. The effort to systematically determine the effect of die gap on UTG extrusion was masked by larger problems of the overall extrusion process, such as bubble "dutch roll".

Test Results

The UTG films extruded were tested by SSS to determine ultimate tensile strength, ultimate elongation, cold brittleness characteristics in liquid nitrogen (-320 degrees F) and general physical properties, such as clarity, optical characteristics and IR scan.

As shown on the attached graphs, all UTG films exhibited the anomaly of increasing strength with decreasing weight. In fact, the per cent increase is remarkable. The thinnest gauge UTG film has almost 300% greater strength than does 1/2 mil gauge film from the same resin family (ultimate tensile strength - 2, 580 psi). Compared to high strength commercial films, such as 1/2 mil VISQUEEN DFD 5500 film, the improvement is also dramatic, over 300% increase in tensile strength.

The ultimate tensile tests were conducted using normal laboratory procedures. Standard film test elements were carefully prepared to eliminate any edge effects. All specimens were 2 in. x 12 in. The samples were inserted in a test machine and loaded in a horizontal, parallel plane with weights. Both the amount of weight and elongation were measured carefully and recorded. At least two samples were tested in each test to verify repeatability.



U.T.G. ANOMALY OF INCREASING ULTIMATE TENSILE STRENGTH WITH DECREASING GAUGE

SELECTED TEST RESULTS: ULTIMATE TENSILE STRENGTH

Gauge	Resin	σ - PSI	Direction	Film Layers
1/16.3	DEX 8028	7,500	M	S
1/16.3	DEX 8028	7,540	M	S
1/16.3	DEX 8028	7,100	M	D
1/16.3	DEX 8028	6,570	M	S
1/16.3	DEX 8028	3,380	T	S
1/16.3	DEX 8028	3,380	T	D
1/16.3	DEX 8028	3,110	T	S
1/16.3	DEX 8028	3,370	T	S
1/13.9	DEX 8028	5,780	T	S
1/13.9	DEX 8028	2,110	M	S
1/14.9	DEX 8025	5,650	T	S
1/14.9	DEX 8025	2,720	M	S
1/12	SSS Std	5,060	T	S
1/12	SSS Std	2,820	M	S
1/9.2	SSS Std	4,700	M	D
1/9.2	SSS Std	1,730	T	D
1/7.5	SSS Std	4,760	M	S
1/7.5	SSS Std	1,750	T	S

M= Machine T = Transverse S = Single Layer D = Double Layer

Theoretical Analysis

The reason for this increased tensile strength is most certainly associated with the greater orientation the film receives in the extrusion process. However, even though the draw ratio is 109, as discussed above, the blow up ratio (2. 55) remained almost unchanged, and yet the transverse tensile strength increased by almost the same ratio. Thus, the greatly increased draw ratio will not explain the increased tensile strength entirely.

Consequently, it is believed that a primary cause of the improvement is due to the greater degree of molecular orientation throughout the entire cross section of the film. The attached graph shows this orientation qualitatively.

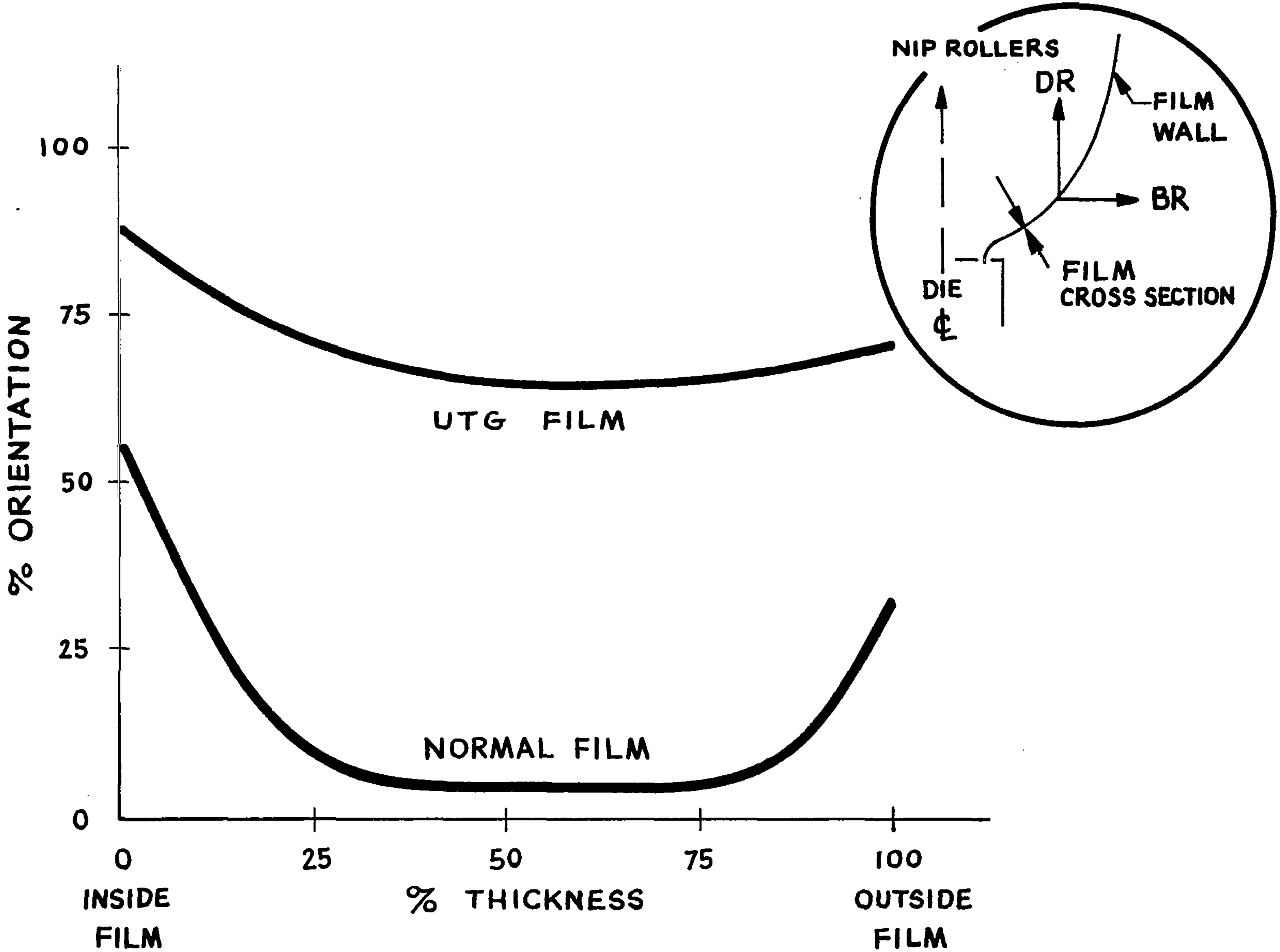
Reference to the chart demonstrates that the film receives more orientation at a critical time immediately after it leaves the hot die and is forced outward at a sharp angle. The amount of molecular orientation across the film thickness then decreases rapidly for normal film, less rapidly for UTG film. All molecules across the film in the UTG material are being "worked", and not just the outer layers. Referring back to the graph, molecular orientation on the opposite side of the film increases again, but much more sharply for the normal film. Consequently, these results verify that the strength of heavy gauge polyethylene film is produced predominantly on the more highly stressed wall and boundary areas.

Elongation Tests

Ultimate elongation characteristics of the film were measured using conventional laboratory methods. Strain was measured and reduced to inches/inch and converted to per cent. The ultimate elongation of the film decreased as shown in the table below:

	Ultimate Elongation %	
	Machine Direction	Transverse Direction
UTG Film*	90	150
Normal Film*	275	400

*SSS Standard Resin



MOLECULAR ORIENTATION ACROSS THE FILM

This decrease in elongation correlates with the increase in strength of the UTG film. The theoretical analysis of these results are discussed below.

Other Tests

Tests in liquid nitrogen verified previous contractor tests that very thin films have excellent flexibility characteristics at cryo-temperatures. The film was tested double thickness, as it comes off the roll, and "twist-flexed" in a LN_2 bath. There were no failures in 50 cycles. This test procedure is considered qualitative in nature only and was done to correlate with the performance of other SSS thin films.

Another unusual test showed that UTG films exhibit stress polarization. Single layers of film were stretched out flat in a circular tensioning device and examined against plain, white light. The material exhibits complete stress polarization, allowing stress patterns to be observed directly in the film.

Infrared scans of blown film samples from each resin were obtained with an IR-4 Beckman Spectrophotometer.This data was presented in the front section of this report, where the results were discussed.

Tentering

Tentering tests, to increase film area and thereby decrease film gauge, were carried out at ambient temperature and at several higher temperatures.

Tests at ambient temperature were run with 1/7 mil and 1/10 mil film extruded from SSS Standard resin. The film was left in layflat tube form. Prior to attachment the film was carefully marked with identifying lines of known length, both horizontally and vertically. The film was secured horizontally in an even plane without stress concentrations at either top or bottom. The lower bar was gradually loaded in a vertical plane, maintaining a loading axis of symmetry through the film. The below table gives the results of these tests.

Material	% Increase in Area During Loading	% Increase In Area After Unloading
1/7 mil	40%	--
1/10 mil	20.8%	14%
1/10 mil	9.4%	5.4%

Higher temperature seemed to impede plastics elongation. In nearly all cases the specimen failed prior to significant elongation. ($100^{o}F$ - $150^{o}F$).

A second approach to tentering was the use of film sealed over a 14.5 inch diameter cylinder and inflated with air pressure. The maximum height that a hemispheric film bubble achieved was 4.5 inches above the initial position. This tentering was executed at both room temperature and in an oven. As the pressure increased, superficial, clear cracks appeared in the machine direction. Quite often expansion proceeded along these cracks to the crest of the bubble, and then failure occurred.

In summarizing the tentering approach, an area increase of 14% could be obtained for UTG films. However, the results were not encouraging with these test methods. In analyzing these results from a theoretical approach, it should be noted that polyethylene film can be as much as 85% crystalline. Low density films such as SSS Standard and the DEX resins are somewhat less crystalline. It is because of such crystallinity that elongation, and significant area increases cannot be obtained. As the film elongates, it becomes more crystalline by alignment of the crystallites. When this happens, strength increases but plasticity decreases. Failure takes place along crystal interface by means of slip planes. A special characteristic of visco-elastic fracture is that the material properties change while fracture occurs. Also, the material properties depend on the rate of fracture progression. As a consequence, the methods of tentering used in these tests are not adequate and need to be improved.

SUMMARY OF RESULTS

Ultra thin gauge film was extruded using special equipments to produce gauges down to 6. 1 x 10^{-5} inch (1/16. 3 mil). The primary problem was bubble "dutch roll" between the die and nip rollers.

Theoretical study and analysis indicates that film gauges down to 1/52 mil should be capable of being extruded, provided mechanical extrusion problems could be overcome. This analysis is based on molecular weight, molecular length and chain branching data.

All experimental resins and the SSS Standard resin were adequate for extruding UTG films, probably down to 1/20 mil gauge. However, mechanical techniques in operating the extruder masked more definitive analysis of the effect of melt index, density, resin additives and die gap.

A detailed analysis of extruder operation and techniques for producing UTG films was made. Equipment recommendations are presented. The principal result in operating techniques was achieving a draw down ratio of 109, a factor of 10 better than normal commercial operation. The blow up ratio was conventional, 2. 55 for the above film and varied between 1. 8 and 3. 2.

The anomaly of increased tensile strength of the film with decreasing weight (gauge) of the material was examined. The increase in strength was approximately 300% over normal 1/2 mil film from the same resin. A good theory to explain this phenomena has been developed.

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